PB-213 782

The Pollution Potential in Pesticide Manufacturing

Midwest Research Institute

prepared for
Environmental Protection Agency

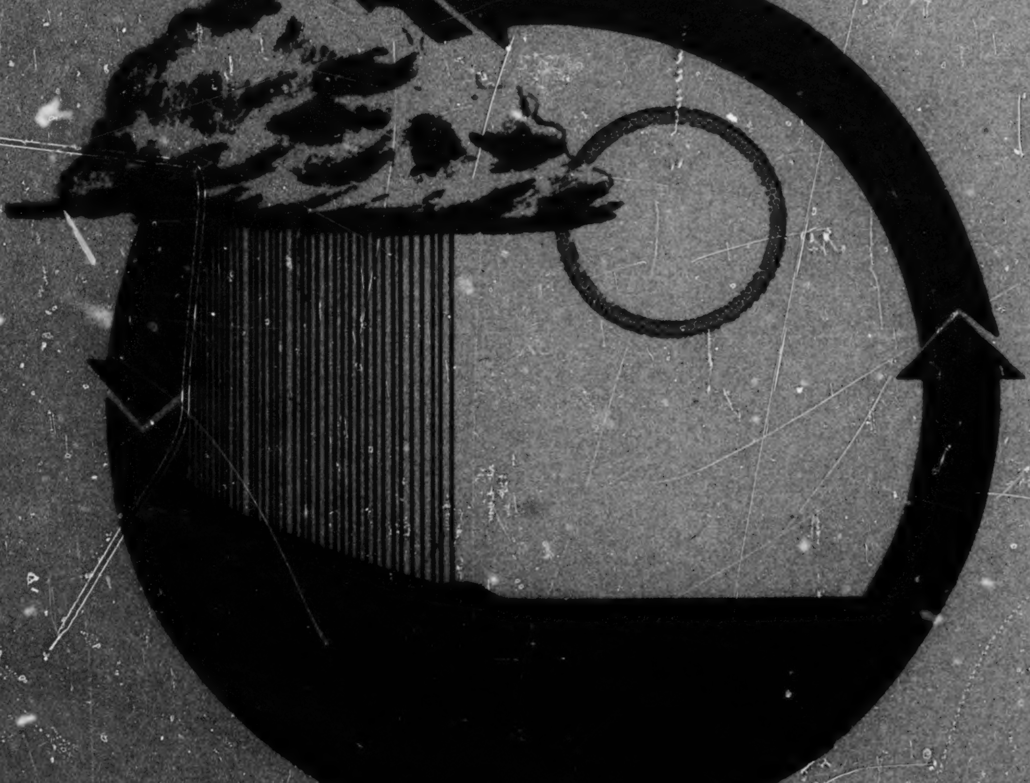
JUNE 1972

Distributed By:
NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

3-257

PB 213 782

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF WATER PROGRAMS



THE POLLUTION POTENTIAL IN PESTICIDE MANUFACTURING

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

276

PESTICIDE STUDY SERIES - 5

THE POLLUTION POTENTIAL IN PESTICIDE MANUFACTURING

This study is the result of
Contract No. 69-01-0142 awarded by the OWP,
as part of the Pesticides Study (Section 5(ℓ)(2) P.L. 91-224)
to Midwest Research Institute.

Edward W. Lawless, Project Leader, M.R.I.
Rosmarie von Rumker, RvR Consultants
Thomas L. Ferguson, M.R.I.

EPA Project Officers were:

Charles D. Reese, Agronomist
David L. Becker, Chemical Engineer

ENVIRONMENTAL PROTECTION AGENCY
Office of Water Programs
Applied Technology Division
Rural Wastes Branch
TECHNICAL STUDIES REPORT: TS-00-72-04

June 1972

EPA Review Notice

This report has been reviewed by the Office of Water Programs of the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, or does mention of trade names or commercial products constitute endorsement or recommendation for use.

PREFACE

This program (MRI Project No. 3556-C) has been under the general supervision of Dr. A. E. Vandegrift, Head, Environmental Sciences Section of MRI's Physical Sciences Division. The project team consisted of Dr. Edward W. Lawless, Project Leader, Dr. Rosmarie von Rümker of RvR Consultants, and Mr. Thomas L. Ferguson, with the assistance of Miss Anne Aspoas, Miss Meredith Reichel and Mr. Edward Trompeter. Dr. L. Eugene Cronin, Dr. Gordon E. Guyer and Mr. T. G. Lewton, Jr., acted as consultants to the program. The assistance of the many members of the pesticide industry who contributed their time and helpful comments to this study is gratefully acknowledged.

Approved for:

MIDWEST RESEARCH INSTITUTE

H. M. Hubbard, Director
Physical Sciences Division

10 January 1972

See page S-1
→ The topics include the following:

TABLE OF CONTENTS

Page

Summary. S-1

I. Introduction. 1

II. History of Pesticide Use and Production 3

A. Discovery of Various Classes of Pesticides. 3
B. Development of Pesticide Use Patterns 20
C. Developments in Manufacture and Formulation Methods . . 26

III. Present Production Volumes and Sites. 39

A. Estimated Production of Major Pesticides. 41
B. Geographical Location of Producers and Transportation Patterns. 54

IV. Modern Manufacturing Methods. 62

A. Criteria for Selection of Pesticides for Case Studies . 62
B. Summary of Classes, Producers, Production, Formulations, and Use Patterns for Case Study Pesticides . . 63
C. Case Studies. 71
D. Summary of Pollution Aspects Based on Case Studies. . . 188

V. Formulation of Pesticides 203

A. Formulation Facilities. 204
B. Pollution Potential in Pesticide Formulation. 205

VI. Marketing of Pesticides 221

VII. Conclusions and Recommendations 230

Appendix A - Toxicity Data on Selected Pesticides. 233

Appendix B - Emergency Procedures in Event of Fire in a Warehouse Containing Pesticides 239

Appendix C - Preliminary Discharge Data Submitted by Pesticide Producers Under the 1899 Refuse Act 243

Appendix D - List of Individual Contributors to This Study 246

Preceding page blank

TABLE OF CONTENTS (Continued)

List of Tables

Table	Title	Page
S-I	Production Volumes of Major Pesticidal Ingredients.	S-3
S-II	Uses, Classes and Production Volumes of Selected Pesticides.	S-5
S-III	Summary of Manufacturing Wastes and Disposal.	S-11
I	Pesticides Produced, Imported or Sold in the United States	10
II	Estimated U.S. Pesticide Production Volume, 1971.	42
III	United States Usage of Wood Preservative, 1965-69	49
IV	United States Imports of Synthetic Organic Pesticides, 1965-69	50
V	United States Exports of Pesticides, 1968-69.	51
VI	Summary of Production Volumes of Selected Herbicides, Insecticides, and Fungicides.	53
VII	Major Pesticide Production Sites.	56
VIII	Pesticide Ratings	64
IX	Uses and Classes of Selected Pesticides	67
X	Selected Herbicides, Estimated Production Volume, Formulation, Uses, and Areas of Use, 1971	68
XI	Selected Chemical Insecticides, Estimated Production Volume, Formulations, Uses, and Areas of Use, 1971. . . .	69
XII	Selected Biological Insecticides, Fumigants, and Fungicides: Estimated Production Volume, Formulations, Uses and Areas of Use, 1971	70
XIII	Case Studies: Summary of Producers Visited	72
XIV	Order of Presentation of Case Studies	73
XV	Summary of Formulation and Warehousing Activities by Key Pesticide Producers	191
XVI	Summary of Packaging and Transportation Practices for Key Pesticides.	193
XVII	Summary of Manufacturing Wastes and Disposal	195
XVIII	Summary of Formulators, Packagers, and Distributors Visited	203
XIX	Aerosol Pesticide Filling Plants.	206
XX	How Pesticides are Moving to Market	213
XXI	Marketing Outlets to the Consumer for Pesticides.	223
XXII	Major Pesticides Sold in the Garden and Home Market	224
XXIII	Types of Containers Used for Garden and Home Pesticides . .	225
XXIV	Number and Types of Containers for Agricultural and Related Pesticide Use	227
C-I	Preliminary Discharge Data Submitted by Pesticide Producers Under the 1899 Refuse Disposal Act	245

TABLE OF CONTENTS (Continued)

List of Figures

Figure	Title	Page
S-1	Production Sites for 22 Major Pesticides	S-6
1	Schematic Description of Pesticide Production and Movement to Consumer, Indicating Potential Pollution Sources	2
2	Classes of Pesticides According to Use	20
3	U.S. Production of Synthetic Organic Pesticides	22
4	U.S. Producers' Sales of Synthetic Organic Pesticides	22
5	Corn Harvested for All Purposes, 1964	23
6	Cotton Harvested, 1964	23
7	Soybeans Harvested for All Purposes, 1964	24
8	Alfalfa Cut for Hay, 1964	24
9	Tobacco Harvested, 1964	25
10	Tomatoes Harvested for Sale, 1964	25
11	Synthesis of Some Chlorinated Hydrocarbons and Related Pesticides	28
12	Synthesis of the Diene Group of Chlorinated Insecticides--From Hexachlorocyclopentadiene	29
13	Synthesis of Phosphorus-Based Pesticides	30
14	Synthesis of Some Carbamate Pesticides	31
15	Synthesis of Triazine Pesticides	32
16	Locations of Pesticide Production Plants	55
17	Production Distribution for 22 Major Pesticides	60
18	Production and Waste Schematic for DDT	75
19	Production and Waste Schematic for Aldrin	81
20	Production and Waste Schematic for Dieldrin	85
21	Production and Waste Schematic for Chlordane	89
22	Production and Waste Schematic for Toxaphene	95
23	Production and Waste Schematic for Disulfoton	100
24	Production and Waste Schematic for Malathion	105
25	Production and Waste Schematic for Phorate	110
26	Production and Waste Schematic for Parathion and Methyl Parathion (Monsanto)	114
27	Production and Waste Schematic for Carbaryl	119
28	Production and Waste Schematic for Aldicarb	124
29	Production and Waste Schematic for 2,4-D (Dow Chemical)	129
30	Charcoal Absorption/Filtration Plant for Treating Phenolic Wastes	135
31	Production and Waste Schematic for 2,4,5-T	137

TABLE OF CONTENTS (Concluded)

List of Figures (Concluded)

Figure	Title	Page
32	Production and Waste Schematic for Atrazine.	144
33	Production and Waste Schematic for Trifluralin	149
34	Production and Waste Schematic for Alachlor.	154
35	Production and Waste Schematic for Captan.	158
36	Production and Waste Schematic for Methyl Bromide (Dow Chemical)	164
37	Pyrethrum Refinery and Waste Schematic (FMC Corp.) . . .	169
38	Production and Waste Schematic for *Bacillus thuringiensis*.	176
39	Production and Waste Schematic for Mercury Chloride. . .	183
40	Acute Oral Toxicity.	200
41	Acute Dermal Toxicity.	201
42	Pesticide Aerosol Filling Plants	207
43	1969 United States Aerosol Container Production.	208
44	Liquid Formulation Process	210
45	Dust Formulation Process	212

SUMMARY

The use of pesticides has become an extremely important factor in the United States and indeed throughout the world in determining man's quality of life. The benefits which have been obtained from this usage--increased production of food and fiber and increased freedom from disease and obnoxious plant and animal life--have not been without some undesirable side effects, such as direct effects on nontarget organisms, the indirect unbalancing of delicate ecosystems, and the environmental contamination by persistent pesticides which may tend to be biologically accumulated in food chains. In addition, the possible long-term effects of low levels of pesticides on man himself is the cause of serious concern. Hence, the entire subject of pesticide production and use is under intensive study by government and nongovernment scientists in the United States and in many other countries.

The production and use of pesticides is not new or even of recent origin. From ancient times man has investigated the minerals, and the plant and animal life around him for their value as medicinals, in the production of his food, in warding off the attacks of obnoxious or dangerous insects, and against his fellow man. A tremendous growth has occurred, however, during the past 40 years in the number of pesticides available, the variety of applications, and the volumes of production of the active ingredients and their formulated products. A broad definition of "pesticides" is used here which includes: rodenticides; insecticides; larvacides; miticides (acaricides); molluscicides; nematocides; repellants; synergist; fumigants; fungicides; aligicides; herbicides; defoliants, desiccants, plant growth regulators and sterilants. On this basis over 1,500 chemical pesticides have been produced. About 275 pesticides are of commercial importance and perhaps as many as 8,000 individual formulated products are prepared for specific uses and methods of application.

The objective of this study was to survey and evaluate the environmental pollution potential associated with the manufacture, formulation, and marketing of pesticides, including such related activities as packaging, transportation and warehousing, i.e., all of the operations up to the point where a pesticide is placed in the hand of the normal consumer.

Pesticide Production Volumes

In order to evaluate the pollution potential of pesticide manufacture, knowledge of current production volumes was needed. A serious handicap here was the unavailability of data on how much of each pesticide is produced or even on which ones are produced in the largest quantities in the United States. Most of this information is in the hands of the U.S. Tariff Commission, but it is not disclosed in a meaningful manner. The Tariff Commission publishes partial production data for synthetic organic compounds which includes a section on pesticides, but the data are categorized and grouped: no data are disclosed for specific compounds unless there are three or more producers (and not even then if one producer is dominant) because these data are considered proprietary by the companies and are revealed in confidence to the Tariff Commission. Under this policy, production data are not now available on the most widely used insecticide (toxaphene) or herbicide (atrazine) and apparently will no longer be available on DDT or 2,4-D after 1970 as only one or two producers of these materials remain. We strongly recommend that public disclosure of production data for pesticides and all hazardous materials be made mandatory, so that scientists, regulatory officials, legislators and other concerned citizens can make use of these data to make an intelligent assessment of environmental impacts and of areas which require further research, new regulations, or legislation. Furthermore, we believe a sizable percentage of the pesticide industry would actually be agreeable to the uniform disclosure of these data, because under the present situation most companies maintain an expensive staff of market researchers to develop much of these data anyway. In addition, some industry members apparently feel that the availability of such data would help relieve their companies of certain guilt--by--association feelings toward the pesticide industry in general.

The production volumes of all pesticides have been estimated on this program. The results for the major pesticidal ingredients are shown in Table S-I, and show that, with the exclusion of the special category (which will be discussed below) the 1.34 billion pounds per year pesticide market is dominated by about 24 major products or product groupings which account for a combined production of 862 million pounds per year or 64% of the market, while the remaining 26% is divided between about 250 other pesticides. Of these, 65-75 are estimated to have production volumes of over 1 million pounds per year.

The special category includes petroleum oils (of which some synthetic and refined products are used directly as insecticidal sprays, but most of which are used more extensively as diluents and carriers and as wood preservatives); creosote and coal tar (general wood preservatives); aromatic solvents; and the dry carriers and diluents. These materials have been of little environmental concern compared to the more active ingredients in most pesticides and are not the focus of the present study (although such materials are deserving of more attention than they have received).

TABLE S-I

PRODUCTION VOLUMES OF MAJOR PESTICIDAL INGREDIENTS[a]

Herbicides		Insecticides		Fungicides		Fumigants/Rodenticides		Special Category	
Product	Quantity	Product	Quantity	Product	Quantity	Product	Quantity	Product	Quantity
Atrazine	90	Toxaphene[b]	50	Sulfur (inorganic)	150	Methyl bromide	22	Petroleum oils[g]	> 1,000
2,4-D	45	DDT	45	Pentachlorophenol and salts[c]	46	Dibromochloropropane	10	Creosote	1,000
MSMA-DSMA	35	Carbaryl	45						
Sodium chlorate	30	Methyl parathion	45	Dithiocarbamate group[d]	40	Other halogenated C_1-C_3 organics[e]	50	Coal tar Aromatic solvents	160 N.A.
Trifluralin	25	Malathion	35	Trichlorophenol and salts	20	Dichlorobenzene[f]	60	Dry carriers and diluents	N.A.
Propachlor	23	Chlordane	25	Captan	18	Warfarin	12		
Chloramben	20	Parathion	15						
Alachlor	20	Aldrin	10						
CDAA	10	Methoxychlor	10						
	—	Diazinon	10		—		—		———
Subtotal	298		290		274		154		———
Total, all pesticides	408		406		297		200		> 2,000

---

[a] Quantity produced in million pounds per year for direct pesticidal use, excludes production for other uses except as indicated.
[b] Includes Strobane-T.
[c] Includes use for termite control and as herbicide.
[d] Includes 11 products.
[e] Includes eight or more compounds.
[f] Includes moth proofing and lavatory-space deodorant usage.
[g] Includes synthetic and refined spray oils, diluents and carriers in formulated products.

Study Approach

The approach used in this survey and evaluation has been to select pesticides, producers, formulators and packagers which would be representative of the industry.

A system was developed in which pesticides were rated on the basis of production volume (present and projected); chemical class and production technology; use pattern (biological activity and major crops); toxicity, including human (acute and public health) and nontarget; persistence and biomagnification; and public or legislative concern. On the basis of these ratings, 22 representative pesticides were selected for intensive study of the pollutional aspects of the manufacturing process. These 22 pesticides are listed in Table S-II along with their use, chemical class, estimated production, mammalian toxicity and relative environmental persistence. The production sites of these pesticides are shown in Figure S-1.

Personal contacts and visits were made with the producers of the 22 selected pesticides and also with 15 formulators and packagers and these were supplemented by review of the literature on production, formulation, packaging and marketing practices.

Special Notes from the Case Studies of Manufacturers

The case studies developed a considerable amount of information on the practices of the pesticide manufacturers which is related to the overall pollution potential. Because of the diversity of processes used for the different pesticides, and the different pollution control practices employed, comparison is difficult, but several aspects are worthy of discussion.

1. Raw materials: The raw materials used for the synthesis of many pesticides are hazardous materials and some pollution potential is inherent in the transportation and handling of materials of this nature. Some of these materials are flammable, some are corrosive and poisonous, and some may be exceptionally toxic to fish if spilled into waters. However, the transportation of these materials are subject to close governmental regulation and the handling practices of the pesticide manufacturers are as good as or better than those of industry in general.

The raw material which is common to the most pesticides is elemental chlorine which is used directly on-site in the production of chlordane, toxaphene, 2,4-D, 2,4,5-T, atrazine, captan, carbaryl and mercuric chloride and is used to prepare raw materials brought in for the production of DDT, aldrin-dieldrin and perhaps also trifluralin and alachlor.

TABLE S-II

USES, CLASSES AND PRODUCTION VOLUMES OF SELECTED PESTICIDES

Selected Pesticides	Fungicides	Fumigants	Herbicides	Insecticides	Chlorinated Hydrocarbons	Triazines	Carbamates, N-Alkyl	Aryl Organo-phosphates	Aliphatic Organo-phosphates	Inorganics	Botanicals	Biologicals	Other	Estimated Annual Production (MM lb/year)	Mammalian Toxicity LD_{50} (mg/kg)	Environmental Persistence
Alachlor (Lasso)			H										X	20	1,200	Low
Aldicarb (Temik)				I			X							2	0.93	Low
Aldrin				I	X									10	55	High
Atrazine			H			X								90	3,080	Low
B. thuringiensis				I								X		1.5	Nontoxic	Low
Captan	F												X	18	10,000	Medium
Carbaryl (Sevin)				I			X							45	540	Low
Chlordane				I	X									25	570	High
2,4-D			H		X									45	500	Low
DDT				I	X									45	113	High
Dieldrin				I	X									0.5	60	High
Disulfoton				I					X					8	2.0-12.5	Low
Malathion				I					X					35	2,800	Low
Mercury fungicides	F									X				0.2	30-200	Low
Methyl bromide		Fu											X	22	21 mg/liter	Low
Methyl parathion				I				X						45	9-42	Low
Parathion				I				X						15	6-15	Medium
Phorate (Thimet)				I					X					8	1.6-3.7	Medium
Pyrethrins				I							X			0.3	1,500	Low
2,4,5-T			H		X									6	300-800	Low
Toxaphene (including Strobane-T)				I	X									50	69	Medium
Trifluralin (Treflan)			H										X	25	> 10,000	Low
Totals (22 pesticides)	2	1	5	14	7	1	2	2	3	1	1	1	4	516.5		

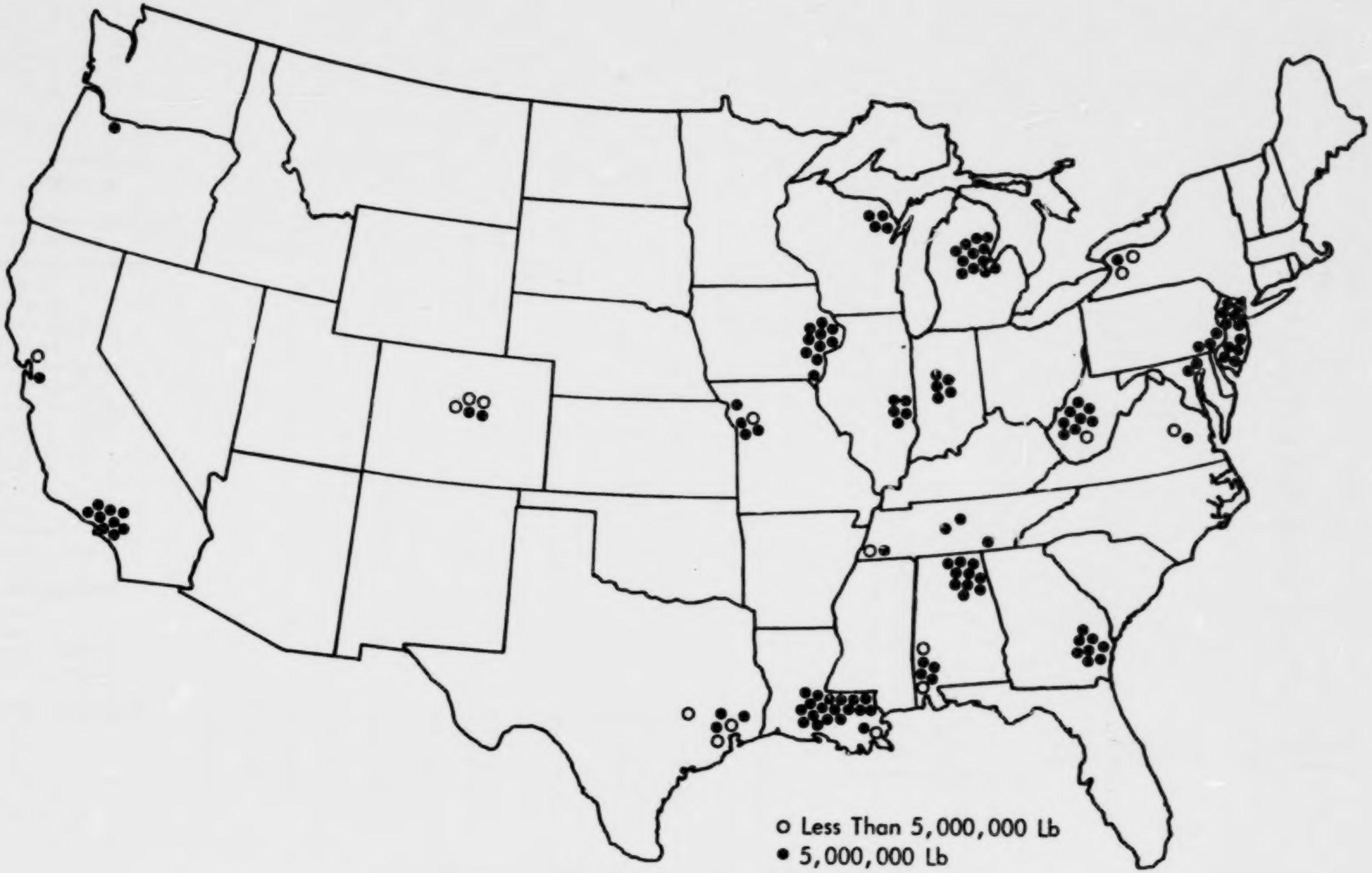

○ Less Than 5,000,000 Lb
● 5,000,000 Lb

Figure S-1 - Production Sites for 22 Major Pesticides

The production of this chlorine formerly involved extensive use of the mercury cells which led to the well-publicized mercury losses. Now, however, these cells are being better controlled and are being displaced by the mercury-free diaphram cells. Only two of the pesticide producers studied here use on-site chlorine generation while the other chlorine users receive it in tank car quantities by rail with the exception of one plant which receives it by pipeline.

Other materials of unusually hazardous nature which are transported by rail, barge or truck include hydrogen cyanide (of which over 10 million pounds are required for atrazine), carbon disulfide, various amines, and the concentrated acids and caustic. The P_2S_5 used in all the organophosphorus pesticides, the C_5Cl_6 used for aldrin, and numerous other materials also pose some hazard.

The raw materials may be stored on-site in bulk storage facilities, but in many cases are drawn directly from the shipping container (e.g., tank car or tote bin) and used in the production processes. The handling of materials such as chlorine are apparently in conformity with good industrial practice codes. Accidental spills of raw materials occasionally occur which require special clean-up and disposal procedures. In many cases scrubbers or dust collection equipment are used in the raw material unloading areas.

2. Production processes: The manufacturing processes for pesticides vary considerably from product to product; but two characteristics are generally present which may differentiate the pesticide industry from many, if not all, of the large industries which are of environmental pollution concern: the ingredients handled or produced have usually high toxicity to some animals (e.g., man or fish) or plant-life; and the production processes normally require only low or moderate temperatures, compared for example, to industries producing ore- or rock-derived products. Because of the toxicity of the materials handled, production facilities were designed to include a great many safety features to minimize occupational hazards. Because of the moderate temperature, air pollution control of good efficiency could be largely adapted from existing technology. Water pollution control, as will be discussed in a subsequent section, poses a much more difficult problem than air pollution in the pesticide industry.

The production plants for the 22 key pesticides studied range from capacities of less than 1 million pounds per year to about 100 million pounds per year and the plant equipment ranges from 1 year old to over 20 years old and in at least two cases the plant buildings are over 50 years old. In general, the more toxic materials such as the organophosphorus and carbamate insecticides and some of the herbicides which have undergone rapid growth recently (such as atrazine) are produced in newer plants, while many of the older chlorinated hydrocarbons and other products are produced in somewhat older equipment. However, almost none of the plants have been designed since the advent of the recent increased consciousness of environmental concern, and most of the companies interviewed have recently completed, are building, or are designing new pollution control equipment to bring their plants into conformity with local standards.

The production equipment is used in almost every case either for only one product or for two very similar products, i.e., two products of the same chemical family and with similar pesticidal applications. Cleanup of equipment is therefore minimized and is small compared to that required in a formulation plant where many products are processed through the same equipment. In cases where solvent cleanup of process equipment is required, the used solvent is generally reused as a matter of economics by recycle to the process, or it may be used in formulation, or combusted for fuel purposes.

Most of the companies interviewed have fairly extensive contingency plans. Many of them maintain a company fire department and others state that they work closely with local fire departments, but this cooperation could probably be improved in nearly all cases.

Good practice dictates that production facilities be diked and that runoff from malfunction, spills, fire extinguishment, etc., can be contained in a holding pond or pit until treated, so that over-loading of the conventional waste treatment plant is avoided. In many, but not all plants, this procedure is in effect.

All the manufacturers of the 22 key pesticides have on-site quality control laboratory facilities and frequently monitor the raw materials and reaction intermediates as well as the final product. In almost no case, it would seem, is a production run of such poor quality or so far "off spec." that it cannot be used--either blended off with a higher quality batch or reworked to remove objectionable impurities.

The efficiency of the synthesis reactions as commercially conducted is generally regarded as proprietary information. Similarly, the efficiencies of recovery of products, by-products and unreacted starting materials are not available. The efficiency of recovery in the past has often depended on the price of the product balanced against the difficulty of recovery, and hence a widely and easily produced material like DDT was previously discharged in sizable quantities. The present trend is toward better recovery and water economy in order to minimize treatment or disposal costs.

3. Storage, handling and shipping: The use of most pesticidal products is seasonal with the major application occurring during the spring

or summer season. Therefore, production and formulation also tend to be seasonal in order to avoid building up undesirably large inventories. Among the manufacturers of the key pesticides studied, several noted that their production peaked in late winter or early spring and some stated that they did not produce during the summer months. On the other hand, most companies do produce the year around and also may formulate on-site so that extensive storage facilities are required. Production site storage in bulk or tank car quantities is sometimes practiced, but long-term storage appears to be more often in drums.

Good storage practices dictate that different pesticides be stored separately, or at least in well-marked locations within a warehouse. In cases where a company handles more than one pesticide at a given location, special care is usually taken to keep herbicides well segregated from fungicides and insecticides, but pesticides which are similar chemically and in activity may be produced in the same equipment and stored in the same area.

The storage facilities of the major producers appear to be generally well regulated to prevent accidental losses of pesticides during handling and storage and well equipped with fire protection. These facilities, however, are not as frequently diked as are the production areas. Similarly, most companies appear to specify such fire protection equipment as automatic sprinklers when they use public warehouses, but few of these warehouses are diked. Thus, warehouse fires which require use of large amounts of water are a serious potential source of pesticide pollution. The further the warehouse is from the control of the primary producer, the greater the potential in an estimated majority of cases.

The mode of transportation of pesticides away from the production sites to the customer, distant storage facility or formulator varies widely because of the variations in location of production sites and use areas. The products are shipped by various combinations of rail and truck, depending on the nature of the material, packaging practices and the marketing structure. Shipping containers range in size from gallon cans and small bags to 6,000 gal. tanks.

The packaging and transportation practices generate different pollution potentials for different products. Most of the highly toxic organophosphates such as disulfoton and the parathions are never shipped in tanks--only drums. Similarly, the toxic carbamates are shipped as 50-lb bags, in the case of carbaryl, and in two specially-modified tank trucks in the case of the extremely toxic aldicarb. The shipment of liquid pesticides (and particularly toxic organophosphates) in drums reduces the potential for a large spill of hazardous material, but the handling and disposal of the emptied drums is a serious problem. On the other hand, most of the toxaphene is shipped in tank cars and trucks and transferred directly into company-owned bulk storage tanks at the formulators' location and no used drums are generated in this step.

A significant difference in pollution potential exists between transport in tank cars and tank trucks. Tank cars are either company-owned or leased by the company from the railroad, and are used over and over for the same or a similar product. If the tank car requires cleaning between shipments or before return to the railroad (as during the slack season), cleanup is done at the production site and wastes go to the company's detoxification or disposal system. Tank trucks, on the other hand, normally are received from the trucking firm in a clean and dry condition, are filled, then transported to the destination and unloaded by the trucker, who then has the responsibility for cleanup before the truck goes to another customer. The trucking firm, however, normally does not have the detoxification and decontamination equipment nor the technical expertise available at the manufacturer. Washings are probably most often disposed in the most convenient manner.

Pesticides which are packaged in cans, drums and bags are very often shipped from the manufacturers only in truck load or car load lots. In many cases, however, as the distribution system fans out, consignment becomes less than car load or truck load lots and the pesticides become part of mixed lot shipments. In such cases the manufacturer loses some control over the product and it may be shipped together with flammable solvents or other material which might increase the pollution potential.

4. By-products and wastes: Virtually every pesticide production process produces aqueous or gaseous streams and frequently solid wastes which contain unreacted ingredients, unrecovered products and solvents, and unavoidable or undesired by-products. Extensive efforts are usually made to minimize by-products and to recover, recycle, or otherwise prevent these process losses from occurring. For each process, however, a balance point is eventually reached between the expense of recovery and the value of the recovered product. In the past, the economic considerations were frequently dominant and process losses were included as unavoidable costs. Under the recent emphasis on environmental contamination further efforts have been made to recover many previously lost materials--even when economics indicated that it was more expensive to do so--and most pesticide manufacturers have invested in or are in the process of building extensive waste treatment facilities wherein those wastes which cannot be recovered are degraded to acceptable levels or disposed by state approved methods. A summary of the principal wastes generated and the disposal methods employed by the producers of the key pesticides is shown in Table S-III.

TABLE S-III

SUMMARY OF MANUFACTURING WASTES AND DISPOSAL

	Liquid Wastes		Solid or Other Wastes	
Pesticide	Source	Disposal	Source	Disposal
DDT	Processing solutions	Evaporative basin	Reactor solutions	County dump
Aldrin	Floor washings, etc.	Evaporative basin	Lime slurry	Lime pit
Dieldrin	Process solutions	Evaporation basin	Filter solids	Incinerate
Chlordane	Process solutions	Deep well	Filter solids	Clay pit
Toxaphene	Pinene-camphene plant	Bio-treatment plant		
	Process solutions	Neutralize, hold, discharge	Filter solids	Solid waste
Disulfoton	Process solutions	Secondary treatment plant	Filter solids, etc.	Commercial landfill
			H_2S	Flare
Malathion	Process solutions	Barge to deep sea	Filter solids	Landfill (with lye)
Phorate	Process solutions	Barge to deep sea	Filter solids	Landfill
			Mercaptan losses	Flare
Parathions	Process solutions	Waste treatment plant	H_2S, S	Flare, incinerate
Carbaryl	Process solutions	Secondary waste treatment	H_2, $COCl_2$, amine	Flare
			Heavy residues	Incinerate
Aldicarb	Process solutions	Neutralize, secondary waste treatment	Process vents	Flare
2,4-D	Process solutions	Trickling filter, biological waste treatment plant	Filter solids and still bottoms	Incinerate, scrub
2,4-D	Process solutions	Charcoal absorption/ filtration treatment	-	-
2,4,5-T	As per 2,4-D			
2,4,5-T	Process solutions	Oxidation pond, discharge	Solids	Landfill
Atrazine	Process solutions	Most to river; some to deep well		
Trifluralin	Process solutions	Biological waste treatment	NO_x	Scrubber
Alachlor	Process solutions	Discharge	Solvent	Fuel
Captan	Process solutions	Hold, discharge	Gas streams	Scrub, vent
Methyl bromide			Gaseous wastes	Scrub, waste treatment plant
Pyrethrin	Aqueous still bottoms	Sewer	Process solids	Storage
			Filter solids	Landfill
Bacillus t.	Process solutions	Sterilized, biological waste treatment	Process air	Incinerate or filter
Bacillus t.	Process solutions	Evaporation pond		
$HgCl_2$ - Hg_2Cl_2	Process solutions	Hg-recovery;	Filter solids	Hg recovery
		Discharge to sewer	NO_x, H_2S	Recovery?

While most of the companies interviewed indicated that they are presently in conformity with local standards, a quantitative picture of the overall pollution potential could not be developed during this program. Under the 1899 Refuse Act Permit program, those companies which discharge to navigable water have been filling discharge data with the Corps of Engineers, but unfortunately, these data started to become available only very late in our study. These data which we have seen, however, indicate that production processes as presently employed for several product lines lead to surprisingly large losses of active ingredients, and toxic raw materials or by-products.

The producers of the persistent chlorinated hydrocarbons use: an evaporative basin, in part* for DDT; an evaporative basin for aldrin and dieldrin; and deep well disposal for chlordane. Therefore, these plants have no discharges subject to the 1899 Act. The evaporative basins require a word of further comment: evaporative and wind blown losses from these facilities require evaluation and the long-term future of the basin should be considered, e.g., what happens if the production site is closed 25 years from now and converted to other uses?

Deep well disposal is used by several pesticide producers in states where that practice is permitted and deep sea disposal is practiced by a number of producers in the eastern seaboard area.

The air pollution aspects of pesticide production are essentially without quantitative data. A small amount of information on levels of certain pesticides in ambient air samples have been reported, but almost no emissions data on specific pesticides from a given plant have been published. These data are much needed.

A number of minor sources of pesticide losses were noted during the interviews. One which has received the attention of a few companies is the small amounts which collect on workers clothing, wipe cloths, etc. Good data on losses on shoes, etc., are simply unavailable, although one company noted that they had reduced miscellaneous losses from 150 to 2 lb/day by increased vigilance to small details. Some companies furnish all production workers with clothing which is then collected and washed or prewashed in a company-run laundry from which the wastewater goes to detoxification treatment. On the other hand, some pesticide producers utilize commercial laundries which may wash the company's materials separately from all others, but do not use any special detoxification treatment. The use of disposal clothing and cloths also requires attention to see that these materials are incinerated rather than go to a landfill if the contaminant is a persistent pesticide.

---

* DDT-containing liquids to go to an approved county Class 1 dump.

Another potential pollution source is contaminated solvents which might be sent to a solvent reclamation service. None of the major manufacturers appear to do this but small producers or formulators may (particularly with solvents used for cleanup purposes). The pesticide content of the solvents may be concentrated in still bottoms or on filter media which are not detoxified.

For some plants the pollution caused by loss of active ingredients is apparently less significant than that caused by unrecovered by-products such as H_2S, which is flared to SO_2, or particulates from fuel combustion, e.g., a plant which produces 10 million pounds per year of most thioorganophosphates could emit over 2 million pounds of SO_2 which would compare with that emitted from a small electric power plant. Depending on the fuel used for process heat and the air pollution controls installed, such a plant might also produce 5 to 10 million pounds per year of particulate pollutants (fly ash, etc.). By comparison, the amount of active ingredient discharged through the waste treatment plant would probably be less than 10,000 lb/year.

The by-product which is common to many pesticide production processes (including chlorinated hydrocarbons, organophosphates, triazines, carbamates, captan, and others) is salt. A large production plant may generate several million pounds per year of salt which with few exceptions is not recovered and is discharged to the river or through waste treatment plants. The effects of these discharges are probably small, but may require further evaluation.

5. Cleanup and decontamination of equipment: Equipment cleanup is an integral part of pesticide manufacture. This operation is both time consuming and expensive, and therefore, is kept to an absolute minimum. Equipment cleanup is generally required for one of two reasons: (1) for equipment maintenance, or (2) for quality control purposes.

Repair and preventive maintenance of production equipment is a continuing process not only because of the types of equipment used, but also in many cases because of the age of the production facility. Corporate philosophy on maintenance varies from scheduled shutdowns of the complete production unit to only unscheduled shutdowns of specific items of equipment for needed repair. Generally, continuous processes require a scheduled shutdown whereas batch operation can be maintained on a less ridged schedule. In either case, the equipment must be emptied of toxic material before it can be opened for inspection or repair.

Quality control necessitates the cleanup of production equipment when the same facility is used for production of different active ingredients to prevent possible cross-contamination. Production scheduling that minimizes the number of product changes is used to reduce this type of cleanup as much as possible. Product changeover usually involves cleanup of only that portion of the process that would contain potential contaminants. Cleanout procedures generally involve flushing the production system with a solvent or in some cases, with steam. Wastes from these cleaning operations normally go into the plant's process-waste system.

The pollution potential associated with equipment decontamination and cleanup is not particularly significant. First of all, only a small quantity of active material is involved in this operation, much less than 1% of the equipment capacity. Of more importance is the fact that wastes generated by equipment cleanup in most cases goes to the plant waste treatment system or in some cases can be recycled to the production unit. Thus, the pollution that could result from discharge of these wastes is primarily dependent on the efficiency of the waste handling system.

6. Safety practices: Safety practices in the pesticide production industry are designed for both the protection of the workers and the containment of highly toxic or dangerous chemicals. The degree and sophistication to which safety measures are used are primarily dependent on the hazard involved.

Two types of pesticides require special environmental control: (1) the organophosphates, and N-alkyl carbamate because of their anticholinesterase activity; (2) the chlorinated hydrocarbons, and inorganics such as mercury because of their stability and persistence. Effects from these, as well as other toxic pesticides, may be produced by swallowing, breathing, or absorption through the skin. Personnel protection measures and devices are designed to minimize exposure.

Coveralls, boots, gloves, goggles, and a variety of respiratory devices are used to protect production workers. In addition, exhaust ventilation systems are used where there is a potential for atmospheric vapor, spray, or dust containing active ingredients, for a hazardous raw material or intermediate. These devices seem to protect personnel from respiratory and dermal routes of intoxication. Protection against ingestion of toxic materials is dependent on demanding high standards of personal hygiene of the individual worker.

The facility for manufacturing aldicarb, one of the most toxic pesticides made in the United States, utilizes highly refined precautions, including air suits for maintenance and decontamination, and glove-cabinets at toxic sample points. Respirators are issued to all personnel who come on the plant site. Less toxic pesticides, such as carbaryl, only require the use of standard personnel safety equipment.

The containment practices and equipment used are also commensurate with the hazard involved. Fire, explosion, and toxicity risks are considered. Control devices commonly used for containment include diking the production area, vacuum operation of process vessels, and caustic scrubbing of process vents.

Medical facilities are a part of the overall safety program found at pesticide plants. Both preventive medicine and first aid services are provided. Typical medical services include a periodic physical examination, first aid for minor cuts or burns, and periodic cholinesterase tests for employees potentially exposed to anticholinesterase pesticides (organophosphates and carbamates).

The potential for environmental damage resulting from inadequate safety equipment and procedures apparently does exist for some facilities; better contingency plans specifically designed to handle emergency situations: fires, explosions, or vandalism are needed for some pesticide production plants.

General Conclusions

1. The major pesticide producers have, on the whole, extensive wastewater treatment facilities. Many of these are new or newly-modified and many are under construction or in design, but some still have little or no effective treatment procedures at some facilities. The disposal of liquid wastes from pesticide manufacture varies widely with different companies, different products, and different geographical locations. Methods being used include: many varieties of neutralization, oxidation, settling, and holding ponds and also secondary and biological waste treatment plants (all of which are followed by discharge to a stream or lake); evaporation basins (which have no outfall); deep well disposal; deep ocean disposal; and incineration. Unfortunately, data on the discharge of effluents to navigable waters are only beginning to become available under the "1899 Refuse Act" for disposal of materials into navigable waters. Pesticide producers were scheduled to submit discharge data to the Corps of Engineers at a time when this study was nearing completion and very little data became available in time to be evaluated. Preliminary review, however, indicates that production processes as presently employed for several product lines do lead to sizable losses of active ingredients, toxic raw materials, by-products, etc., and that these are often not detoxified by the waste treatment facilities, e.g., discharges of active ingredients range from a few pounds per day to over 1,000 lb/day for some products. These data clearly show the need for a systematic study of the scope and effects of these discharges for all producers. On the other hand, four of the major persistent chlorinated hydrocarbon insecticides are now produced in facilities

which do not discharge liquid wastes to a river, i.e., they are using evaporative basins, deep well, etc. The evaporative basins pose two problems which we recommend receive further study: (a) what are the long-term losses of persistent pesticide by evaporation and wind? and (b) what is the disposition of the slowly accumulating sediment or sludge (which is probably highly contaminated with pesticide) in event of periodic cleanout over the years, or in event that the pesticide production is discontinued and the area used for other purposes? In the case of one major chlorinated hydrocarbon, toxaphene, better analytical techniques are needed to establish whether it is persistent, because wastes from this production plant are discharged.

2. The production processes have numerous potential sources of pollution in addition to the primary liquid waste streams, including air emissions, solid wastes, and miscellaneous liquid wastes. The major producer appear to be cognizant of these sources and exercise controls to satisfy local requirements. In a number of cases solid or liquid wastes containing active ingredients go to approved landfills or other burial sites without detoxification, e.g., a liquid waste which apparently contains DDT goes to an approved Class 1 dump in California. At a few facilities high efficiency incinerators are used to dispose of such wastes and we recommend this practice.

Data on air emissions of pesticides are not yet available from production plants and are much in need. The major producers have expended much effort to install baghouses, scrubbers, and other air pollution controls, but data on loss of active ingredients through these devices are needed.

3. Some of the biggest sources of pollution from the major manufacturers are not from the active ingredient (i.e., the pesticide) but from unrecovered by-products such as H_2S (which may be flared to SO_2). Particulate or gaseous pollutants from incomplete combustion of fossil fuel may be bigger sources of pollution than loss of active ingredient for some plants.

4. Nearly all of the basic facilities and equipment now in use for pesticide manufacture and formulation were designed and built prior to the present age of intense concern about environmental quality. Even in the case of one large, completely new facility which has just recently come on stream, additional pollution control procedures and systems had to be added on after the basic plant was designed in an attempt to meet new and higher standards. This situation is not unique to the pesticide industry, but prevails with most manufacturing facilities and processes currently in use. However, this problem is of special importance in the pesticide industry because this industry produces biologically active chemicals which are apt to have higher potential for causing environmental damage than do the effluents discharged from most manufacturing processes.

Numerous examples were noted wherein companies have recently modified their production and waste disposal facilities to decrease the amounts of wastes generated or lost; e.g., improved recycle, recovery and decontamination of by-products, use of lined settling basins to avoid seepage, etc.

Most of the production equipment is dedicated to one product or to two very similar products so that cleaning wastes are minimal.

A host of smaller potential pollution sources were noted some of which have received attention by some producers, but not by others, e.g., carryout of pesticides on shoes and clothes are prevented by sending company-provided work-wear along with wipe cloths, etc., to special laundries, followed by recycle or detoxification of the wash liquid; wash basin or lavatory wash water is sent to the waste treatment plant rather than discharged with sanitary wastes; and the proper disposal of "bottoms" from solvent recovery operations.

5. The formulation of pesticides is probably a larger source of environmental pollution than is the initial production. The formulation is done in some cases by the manufacturer at the production site, but in most cases it is not. A host of formulators process hundreds of pesticides into thousands of finished products. By the nature of this arrangement many of the formulators have relatively small facilities and many of the formulation runs are relatively short. The combined result is that formulators with few exceptions have less extensive waste treatment facilities than do the manufacturer, but they generate considerably more wastes from equipment cleanup. However, the majority of the formulators probably send liquid wastes to municipal sewer systems so that no data are becoming available on the amounts discharged. These smaller businesses are also more apt to send pesticide-containing solvents to commercial solvent reclamation services (where the fate of the pesticide is uncertain) than is the manufacturer.

One problem faced by pesticide formulators wishing to improve their pollution abatement systems and procedures is the lack of authoritative, practical information on how to accomplish this. Several formulating companies whom we interviewed expressed disappointment and dissatisfaction with engineering firms to whom they had turned for help in developing practical systems and procedures which would meet the environmental quality standards set by local, state and/or federal regulatory and enforcement agencies.

A closely related problem is that of dealing with catastrophes. While most basic pesticide manufacturers (especially those where the pesticide production is integrated into a larger chemical manufacturing complex) have emergency procedures, contingency plans on how to handle emergencies such as fires, explosions, floods, etc., were inadequate or absent in most independent pesticide formulating plants and also in many public warehouses which handle concentrated pesticides. Recent history indicates, however, that emergencies in which large quantities of toxic materials are suddenly released into the environment can and do occur.

We therefore conclude that there is an urgent need for the development of principles and procedures by which pesticide formulating and warehousing enterprises can minimize or completely eliminate the release of toxic chemicals into the environment, especially into waterways. Such information is needed (1) for their normal operations, and (2) for emergencies. We recommend that early steps be taken to develop and furnish this type of information to the pesticide formulating industry and to those involved in warehousing large quantities of pesticides.

6. The transportation of pesticides, as with many other products, causes increased chances of accidental breakage, spills and losses. The potential is probably higher in the case of concentrated active ingredient than it is with more dilute formulated products, but varies with the packaging and shipping practices. Overall, the pesticide industry has had relatively few major spills, but the potential remains inherent in the transportation of hazardous materials.

Of smaller scope, but of importance we believe, is the increased pollution potential of tank trucks over railroad tank cars in regard to cleanout procedures: cars are frequently dedicated, require only occasional cleanout, and this is done at the manufacturer's site with wastes going to treatment; the trucks are most often leased one-way and are cleaned by the operator at a point remote from detoxification facilities.

Another important pollution point related to the need to transport pesticides is the inability to empty the standard 5 and 55 gal. metal drums completely. These drums may often be reused for formulated products, etc., and losses at the manufacturer/formulator/packager level are not nearly so large as those at the consumer level; but new designs are needed which permit complete drainage.

7. The warehousing of finished pesticidal products and the marketing of pesticides are a smaller source of pollution, but losses in this area are frequently disposed to the nearest sewer or trash can.

8. Overall the environmental impacts from pesticide manufacturing/formulating/packaging/marketing activities appear to be small compared to those resulting from consumer use of these products; but those negative impacts of the former activities have zero benefit/cost ratios and should be minimized. On the other hand, the costs of reducing all pollutants

to zero are very large; regulations and legislation in this area must consider that unrealistic standards in this area will drive many small producers from the industry and preclude the entry of others who would previously have entered. The large producers generally already have a very large investment in pollution control equipment, will be best able to meet the most stringent control regulations, and will probably do so (with added costs passed on to the buyer) if the product involved is much in demand by the public.

I. INTRODUCTION

The use of pesticides has become an extremely important factor in the United States and indeed throughout the world in determining the quality of life of man. The benefits which have been obtained from this usage--increased production of food and fiber and increased freedom from disease and obnoxious plant and animal life--have not been without some undesirable side effects, such as direct effects on nontarget organisms, the indirect unbalancing of delicate ecosystems, and the environmental contamination by persistent pesticides which may tend to be biologically accumulated in food chains. In addition, the possible long-term effects of low levels of pesticides on man himself is the cause of serious concern. Hence, the entire subject of pesticide production and use is under intensive study by government and nongovernment scientists in the United States and in many other countries.

The Environmental Protection Agency of the United States is currently conducting numerous studies on aspects of the production, use and effects of pesticides of which the study performed under the present contract is one. The objective of this study was to survey and evaluate the environmental pollution potential associated with the manufacture, formulation, and marketing of pesticides, including such related activities as warehousing, transportation and testing, i.e., all of the operations up to the point where a pesticide is placed in the hand of the normal consumer. Emissions of pesticides or other pollutants from these sources to the environment are without the benefits accompanying normal use patterns; they may have detrimental effects and should be minimized. The scope of this study is illustrated in Figure 1.

In the present study, a broad definition of "pesticides" has been used which includes: rodenticides; insecticides; larvacides; miticides (acaricides); molluscicides; nematocides; repellants; synergist; fumigants; fungicides; aligicides; herbicides; defoliants, desiccants, plant growth regulators and sterilants.

Over 275 pesticides are of commercial importance and perhaps as many as 8,000 individual formulated products are prepared for specific uses and methods of application. The brevity of the present study (6 months) precluded, of course, the investigation of all of these pesticides, formulations and products. The approach has, therefore, been to select examples which are representative of the diverse production, properties and use patterns and to investigate these in as much detail as time and resources would permit.

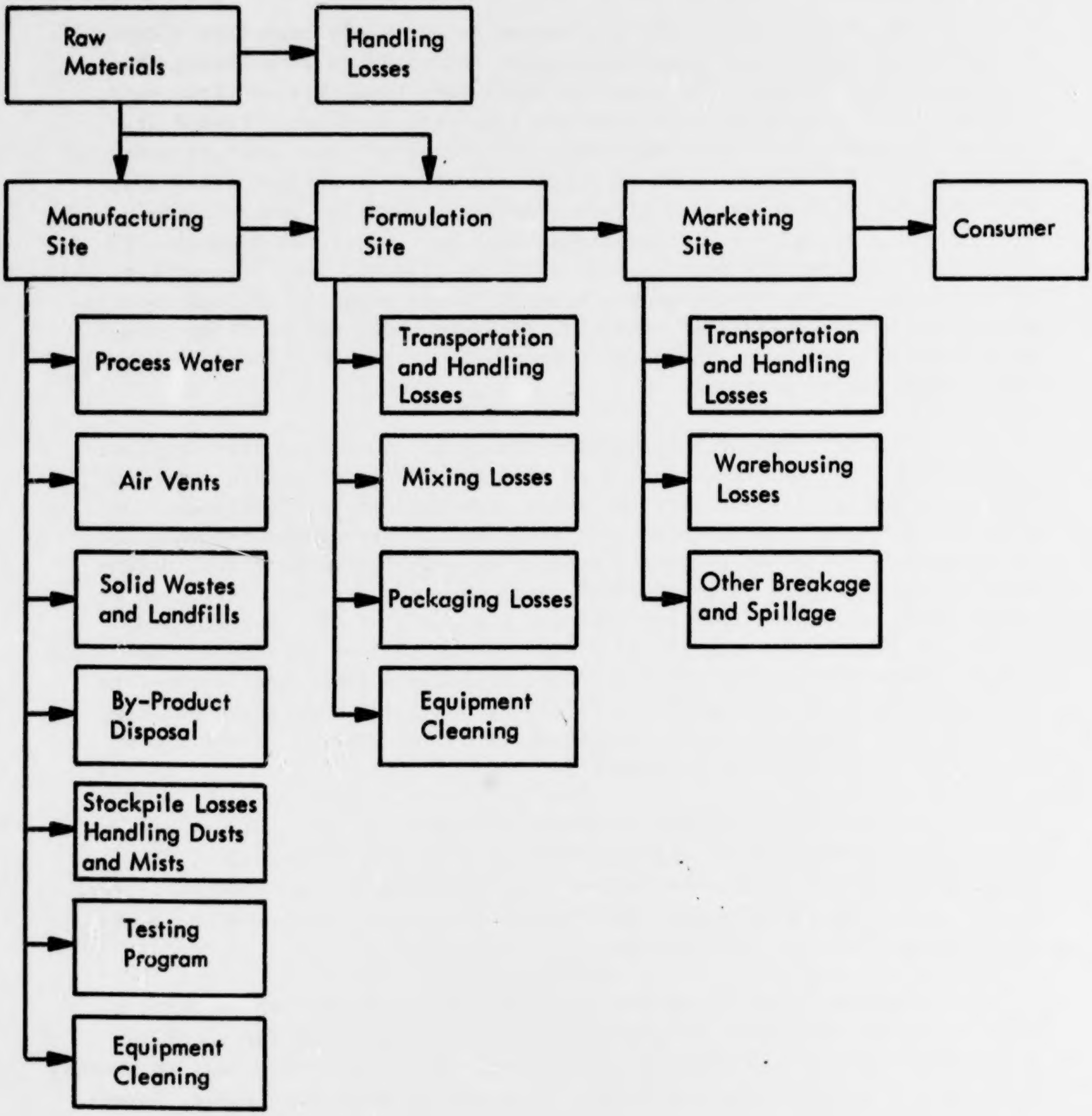

Raw Materials
Handling Losses
Manufacturing Site
Formulation Site
Marketing Site
Consumer
Process Water
Air Vents
Solid Wastes and Landfills
By-Product Disposal
Stockpile Losses Handling Dusts and Mists
Testing Program
Equipment Cleaning
Transportation and Handling Losses
Mixing Losses
Packaging Losses
Equipment Cleaning
Transportation and Handling Losses
Warehousing Losses
Other Breakage and Spillage

Figure 1 - Schematic Description of Pesticide Production and Movement to Consumer, Indicating Potential Pollution Sources

II. HISTORY OF PESTICIDE USE AND PRODUCTION

The production and use of pesticides are not new or even of recent origin, but a tremendous growth has occurred during the past 40 years in the number of pesticides available, the variety of applications, and the volumes of production of the active ingredients and their formulated products.

A. Discovery of Various Classes of Pesticides

From ancient times man has investigated the minerals, and the plant and animal life around him for their value as medicinals, in the production of his food, in warding off the attacks of obnoxious or dangerous insects, and against his fellow man.[1-5] Rotenone (the active ingredient in the roots of *Derris* and other members of the Leguminosae family) was used for many centuries in the Far East and South America to kill fish for easier harvest and against insects. Pyrethrum (from the flowers of *Chrysanthemum cinerariaefolium*) used in the Middle and Near East as an insecticide, Sabadilla (from the bulbs of sea onion) used in South America to kill lice, red squill (from the seeds of *Schoenocanlum officinale*), a rodenticide, and numerous other minor pesticides have been used since ancient times.

The advent of global navigation and travel brought knowledge of many of these pesticides for the first time to Europe, where coincidentally the study of chemistry was developing. White arsenic (As_2O_3) was apparently introduced to Europe from China in the 16th Century as a rat poison and a 1681 text described the use of arsenic as an ant poison. A method of preparing elemental arsenic was published as early as 1649. (Arsenic poisoning of humans was also practiced during this time and may have been used much earlier.) Tobacco was introduced from the New World in about 1550 and a tobacco extract was used as an insecticide on plants by 1690. Nicotine, the active ingredient, was of chemical interest as early as 1571 and was isolated in 1828. Pyrethrum was introduced to Europe in 1828 (or earlier by some accounts) and Rotenone was recognized by 1848 as an effective insecticide on caterpillars. Petroleum oil as an insecticide was mentioned as early as 1787, but the general use of distillates of oil, wood and coal did not develop until 75-100 years later. The use of copper sulfate as a fungicide dates to about 1807.

The latter half of the 19th century saw considerable development in the use of pesticides. In 1854, the insecticidal properties were described of carbon disulfide, apparently the first fumigant. Paris Green, a copper acetate arsenite and probably the first organometallic, and the first example of a "second generation" pesticide, was introduced in

1865-1867 for control of the Colorado potato beetle which was invading the Midwest. A number of other pesticides containing heavy metals was introduced in the late 1800's: London Purple, a complex calcium arsenate mixture with Rosanilline dye, Bordeaux mixture (copper sulfate plus slaked lime) was introduced as an improved fungicide in 1885; copper sulfate was used as a selective herbicide in 1895; mercuric chloride was first used for crop protection in 1891; lead arsenate was introduced in 1892 against the gypsy moth in Massachusetts; sodium fluoride was introduced in 1896 for use on ants and cockroaches (and was subsequently used on many insects and rodents); and borax was apparently introduced as a mild antiseptic and fungicide. Lime sulfur (calcium polysulfide), which was probably present in an insecticidal mixture used as early as 1833, was introduced as a fungicidal solution in 1851 in France and was introduced in California as a sheep-dip and in 1886 as a spray insecticide against San Jose scale.

Kerosene, which had become widely used as an illuminant, was used in 1865 (and in the form of an emulsion with soap in 1877) as an insecticide. Crude oil was used as dormant and summer spray oils in 1897, although the highly refined oils of low phytotoxicity soon became preferred. The creosotic tar oils were used as wood preservatives as early as 1890.

The first synthetic organic insecticide, dinitro ortho-cresol (as the potassium salt), was described in 1892 in Germany

Hydrogen cyanide was used as an insecticidal fumigant in 1886 and formaldehyde, which was introduced as a disinfectant in 1888, was described as a seed disinfectant (insecticidal and fungicidal) in 1896. A host of natural and synthetic organics was apparently examined as pesticides during this period. The most important pesticides during this period appear to have been the arsenicals and nicotine.

The first three decades of the 20th century saw an extension of and building on the developments of the late 19th century, with some emphasis on fumigants and herbicides. Naphthalene (which had been isolated from coal tar in 1820) came into use as a moth-proofing fumigant followed by paradichlorobenzene in 1913. Carbon tetrachloride, described in 1908 as a fumigant for nursery stock, was the first chlorinated hydrocarbon insecticide. Propylene dichloride (1925), ethylene dichloride (1927), and dichloroethyl ether (1929) were also described as insecticidal fumigants for stored crops. Calcium cyanide, introduced in 1923, as a solid source of HCN, is used as an insecticidal and rodenticidal fumigant. Sulfuric acid (1909), sodium chlorate (1910), and calcium cyanamide (which has been introduced in 1905 as a fertilizer) were used as total herbicides.

A number of complex fluorides were described as pesticides during the early 1900's including the naturally occurring cryolite in 1929. Chloropicrin was patented in 1908 as an insecticide, as was a rotenone extract in 1912. The use of the first organomercury pesticide,chlorophenol mercury, dates from wheat bunt application in 1914, and methoxymethyl mercuric chloride (1928) and mercurous chloride (1929) were introduced as replacements for the highly toxic mercuric chloride. Copper napthenate became used as a wood preservative during this time. A trend toward chemical modification of the original pesticide was evident.

The 1930's saw several significant developments which set the stage for the explosive growth of the pesticidal industry which followed. The insecticidal activity of methyl bromide was reported in 1932 (it is now a widely used fumigant for soil and stored products) and illustrated the use of substitutive organic chemistry to yield a product of greater activity and improved physical properties. Aluminum phosphide, introduced in the early 1930's as an insecticidal fumigant for stored grains (it hydrolyzes in moist air to give phosphine gas), and zinc phosphide, a rodenticide bait poison (it hydrolyzes in the rodent's stomach), were the first pesticidal phosphorous containing compounds. In about 1934, research was also starting by Schrader in Germany on the organophosphorous chemistry which would lead to the organophosphate class of pesticides. In the early 1930's also the Du Pont company introduced Ziram (zinc dimethyldithiocarbamate) the first example of a new class of fungicides. Another significant development was the introduction of the pentachlorophenol as a wood preservative in 1936 followed by applications of chloranil (fungicidal crop protection) in 1937 and pentachloronitrobenzene fungicide. Dinitro ortho-cresol (DNOC) was also introduced in 1932 as a herbicide (a forerunner of the 2,4-D family), and pentachlorophenol was introduced as a herbicide by 1940. The first organic thiocyanate insecticide was introduced in 1932 (as Lethane 384) by the Rohm and Haas Company. Phenothiazine, first synthesized in 1883, was discovered to have insecticidal properties in 1934 (plus fungicidal properties a few years later). By 1944, the organic thiocyanates and phenothiazine were being produced in quantities of 6 and 3.5 million pounds per year, respectively. Several other organosulfur and organonitrogen compounds were evaluated during this period, including the first anilide (salicylanilide) introduced as a selective fungicide (mildew) in 1931. Finally, the introduction in about 1939 of the dialkyl phthalates (long known as plasticizers) as repellants for biting insects represented another new step. The total sales of synthetic organic pesticides in the U.S. in 1940 was only 287,150 lb.

A host of heavy metal salts and compounds were also examined during this era, many of which received some pesticidal use, including compounds of thallium, zinc, selenium, barium, chromium and antimony. The chlorate, arsenite and thiocyanate herbicides also came into use during this period as did borax for mold prevention. Of considerable interest in light of current environmental concern was the introduction in Sweden in 1938 of the organomercury compound, Panogen, for seed treatment (although this material was not used in North America until 1949).

Modern Insecticides

In 1939, the Swiss chemists Paul Muller and coworkers at J. R. Geigy A-G discovered, during a search for moth-proofing chemicals, the remarkable insecticidal properties of 2,2-bis(p-chlorophenyl)trichloroethane, a compound which had been first synthesized in 1874. This discovery of DDT, for which Muller was awarded the Nobel Prize in 1948, followed by the development of low-cost production methods in 1943, and the wartime needs, led to an unprecedented acceptance and growth of a pesticidal product. The production of DDT reached 180 million pounds in 1963 in the United States and it was also produced in Europe, in India (where production passed 35 million pounds in 1967),[6/] and apparently in the USSR and in China. Yet, this very volume was, of course, to lead to trouble as DDT residues persisted long after use and spread throughout the world to the extent that a gala centennial in 1974 seems improbable, to say, the least.

The discovery and success of DDT also spurred intensive research of similarly structured chemicals, and of chlorinated hydrocarbons in general. Insecticidal properties were discovered in 1941 in France and in England in 1942, for benzene hexachloride, which had been known since 1825. The discovery that the γ-isomer (four isomers had been known since 1912) had exceptional potency lead to methods of its synthesis (lindane) and to a focusing by organic chemists of the study of structure-activity relationships. Production of BHC also reached over 110 million pounds in 1951, but production declined rapidly after 1956. Methoxychlor, the most widely used of the DDT analogs and a compound known since 1893, was discovered to have insecticidal properties in 1944, along with DDD and with the difluoro-analog (DFDT) at about the same time in Germany. Numerous other DDT relatives were synthesized and tested during the late 1940's and early 1950's and a dozen or so were produced commercially. With the subsequent decline in popularity of DDT itself, interest has been revived in the present day in finding active derivatives which are not persistent and which do not biomagnify in the environment.

The second major family of pesticides which emerged from wartime research was the phenoxyalkanoic acid herbicides of which 2,4-D became the most widely used. An analogue, 2-methyl-4 chlorophenoxyacetic acid (MCPA), discovered at about the same time, was apparently used in England in 1941-1942 and was produced commercially by Imperial Chemical Industries in 1945. The 2,4-D, apparently held under secrecy for military reasons, was patented as a growth stimulant, interestingly enough, in 1943 and as a herbicide in 1945. Production was started in 1944 by Amchem, passed 20 million pounds in 1949, and over 100 million pounds per year (acid equivalent of esters and salts) by the late 1960's. Of the dozen or more other chlorophenoxy herbicides that have been developed only 2,4,5-T (introduced in 1944) has reached large production volume, although Silvex and 2,4-DB are of commercial importance. Unlike DDT and BHC, the 2,4-D family is nonpersistent in the environment.

Several other pesticides worth noting also were developed during the war including: the rodenticides, sodium fluoroacetate (extremely toxic to mammals, but a natural constituent of some African plants), and warfarin, an anticoagulant of low acute toxicity (1944); the herbicides; the metal-dithiocarbamate (=NC(S)S- group) fungicides: Ferbam, Nabam and Zineb; several halogenated fumigants; the repellant, ethyl hexanediol (6-12); the synergist, piperonyl butoxide (1947); and the herbicides trichloroacetic acid, TCA (1944); and ammonium sulfamate (1945).

Immediately following the end of World War II several new classes of pesticides became available including: the aldrin-toxaphene group of highly chlorinated organics; the organophosphates; the carbamates; and the substituted ureas.

In 1945-1946, chlordane and heptachlor, the first two of the highly chlorinated organic insecticides derived from hexachlorocyclopentadiene, were announced by Hyman of the Velsicol Company and discovered independently by Riemschneider in Germany. These were quickly followed by numerous related compounds including aldrin, dieldrin and endrin in 1948 and the structurally related toxaphene, which was prepared by chlorination of camphene at Hercules in 1947. About 16 members of the toxaphene-aldrin group have been produced commercially. About 35 other chlorinated aromatics and aliphatics are produced.

A major new class of insecticides which became available at the end of World War II were the organophosphorus compounds, a development assisted considerably by German research under Gerhard Schrader on anticholinesterase chemical warfare agents. The first of these (patented as an insecticide in 1942, in Germany, and surprisingly enough in 1943 in the U. S) was identified, after some early confusion, as TEPP (tetraethylpyrophosphate) a compound first prepared in 1854. This relatively simple ester was rapidly followed by the synthesis and commercialization in the U. S. and Europe of a number of phosphorus compounds which incorporated different structural features: the phosphoramide, (P-N bonds), Schradan; the thiophosphates (P=S bonds), parathion (1947), methyl parathion (1949), diazinon (1953), and demeton; the dithiophosphate, malathion (1950); the thiophosphono compound (C-P=S grouping), EPN (1950); and the alkyl thiodithioate, phorate (1953). Over 80 organophosphorus pesticides have been described to date.

Several classes of nitrogenous pesticides have been produced since 1945. Herbicidal activity was discovered in 1946 for substituted ureas and a series of "urons" were introduced subsequently (largely by Du Pont), including: monuron (1952); diuron (1954), fenuron (1957), chloxuron (1960), and noruron (1962). Included in this general category also might be a number of (a) herbicides: hydrazides, e.g., MH (1948 by U. S. Rubber), amides, e.g., CDAA (1956, Monsanto); anilines, e.g., propanil (described in 1951, commercialized in 1960); and alachlor (1966); and uracils, e.g., bromacil (1963, Du Pont); (b) fungicides: imides, e.g., cycloheximide (1949, Upjohn) and the two trichloromethylthio imides captan and folpet (1949, Standard Oil); a guanidine, dodine (1956, American Cyanamide); and (c) repellants: an amide, diethytoluamide (1955, Hercules). About 50 pesticides are included among these. In addition, about 35 other compounds which contain amine, amidine, diazo, azole, imidazole, pyridine, quinoline, diazine, thiazine or nitrile functions have been produced as pesticides (most are herbicides or fungicides; a few are insecticides). Of these picloram with a production of about 5 million pounds per year is probably the most significant commercially. About six herbicidal quaternary ammonium salts are available of which the imported diquat and paraquat (introduced in 1958) appear to be most popular. Three other classes of nitrogenous compounds require special mention because of the production volumes and variety: the carbamates, the triazines and the nitroaromatics.

The carbamates have about the broadest range of biological activity known for any chemical class of compounds. The toxicity to mammals and plant growth regulating properties of some members of this family were known before 1930. The N-aryl carbamate (Ar-NH-C(O)-OR group) ester, propham (IPC) was commercialized in 1945 as a selective herbicide (grasses), followed by the chloro derivative in 1951. A series of thiocarbamate herbicides such as EPTC was introduced by Stauffer Chemical in 1954, and several other herbicidal and fungicidal carbamates of various structures have been introduced more recently. The insecticidal (chlorinesterase inhibiting) N-alkyl carbamates were patented first in 1952, but the most important today are carbaryl (1956), propoxur (1959), aldicarb (1965), methomyl (1966), carbofuran (1967), and Bux Ten (1968). About 32 carbamates, eight thiocarbamates and eight dithiocarbamates (including the metal complexes) have been produced.

The first example of the triazine class of pesticides was a fungicide introduced experimentally in 1955 by Ethyl Corporation and now known as Dyrene. The major entries in the field, however, are the herbicides introduced by the Geigy Company including: simazine (1956), atrazine (1958), propazine (1960), ametryne (1969) and others. Production of atrazine in the U. S. may soon pass 100 million pounds yearly.

As previously noted, DNOC has long been known to have insecticidal and herbicidal properties. Several other nitrophenol derivatives have been developed as pesticides including the herbicide, dinoseb (1945 et. seg., Dow) and the acaracides dinocap (1946, Rohm and Haas), binapacryl (1960), dinobuton (1963), nitrofen (1964), fluorodifen (1968), and others. The nitroaniline herbicides, dichloran (1959), trifluralin (1960), benefin (1965), and nitralin (1966) have been of more commercial importance with total production of perhaps 40 million pounds.

The chlorinated benzoic acid family of herbicides was introduced in 1954 with the 2,3,6-TBA of Heyden Chemical and the polychlorinated acid of Du Pont. The amino dichloro derivative, chloramben introduced by Amchem Products in 1958 is the leader in the field today, with an estimated yearly production of 20 million pounds, followed by dicamba (1965), dacthal (an ester, 1959) and the acetic acid analogue of 2,3,6-TBA, chlorfenac (1959).

Other herbicides of interest include the organic arsenicals introduced by Ansul Chemical in 1958 and the host of organic mercurials introduced primarily as fungicides, although phenyl mercury acetate was used as a selective herbicide (crabgrass) as early as 1947. Certain organotin compounds have also been recently introduced.

Considerable interest has recently developed in newer methods of pest control which do not center on synthetic organic chemicals. These include Bacillus thuringiensis, which has been known since 1915, but introduced as a microbial insecticide (Lepidoptera larvae) in 1960, polyhedrosis virus, juvenile hormone, and other experimental pesticides.

The pesticides and related products which are currently produced in or imported into the United States are listed in Table I. The pesticides are grouped by use class (herbicide, insecticide, fungicide, etc.) and arrangement is alphabetical by common name or in some cases, by tradename.

TABLE I

PESTICIDES PRODUCED, IMPORTED OR SOLD IN THE UNITED STATES[a]

A. Herbicides and Plant Growth Regulators

Pesticide	Producer[b]
Alachlor (Lasso®)	Monsanto
Ametryne®	Geigy
Ammonium Sulfamate	Du Pont
Arsenicals, organo	
DSMA	Ansul, Cleary, Diamond, Dow
MSMA	Ansul, Diamond, Vineland
MAMA	Ansul
CMA	Vineland
Dimethylarsinic acid (cacodylic acid)	Ansul, Vineland
Arsenic acid	Pennsalt, FMC
Atrazine (AAtrex®)	Geigy
Bandane®	Velsicol
Barban	Gulf
Benefin	Lilly
Bensulide	Stauffer
Bentanal® (phenmediphan)	Imported
Borax (sodium tetraborate)	Am. Pot., U. S. Borax
Bromacil (Hyvar®)	Du Pont
Bromoxynil	Imported
Butylate	Stauffer
CDAA (Randox®)	Monsanto
CDEC (Vegadex®)	Monsanto
Chloramben (Amiben®) and derivatives	Am. Chem.
Chloroxuron	Geigy
Chloropropham	PPG
Cycloate	Stauffer

---

[a] Based on U. S. Tariff Commission data for 1970, on 1969 data from the Pesticide Review, 1970, and other sources.

[b] For complete company names see page 56 .

TABLE I (Continued)

A. Herbicides and Plant Growth Regulators (Continued)

Pesticide	Producer
2,4-D (acid, esters, and salts)	Dow, Chipman
Dalapon	Dow
DCPA (Dacthal®)	Diamond
Def®	Chemagro
2,4-DEP	Uniroyal
Diallate	Monsanto
Dicamba	Velsicol
Dichlobenil	Imported
Dinitrobutylphenol (and derivatives)	Dow, FMC
Dinitrocresol	Imported
Sodium salt (DNOC)	FMC
Dinoben (acid and derivatives)	GAF
Diphenamid	Arapohoe, Upjohn
Diquat	Imported
Diuron	Du Pont
DMSA (N-dimethylamine succinamic acid)	Uniroyal
Endothal	Pennsalt
EPTC (Eptam®)	Stauffer
EXD (ethylxanthogen disulfide)	Roberts
Fenuron	Du Pont
Fluometuron	Ciba
Folex®	Mobil
Gillerellic acid	Abbott, Merck
Indolebutyric acid	Merck
Lenacil (Venzar®)	Du Pont
Linuron	Du Pont
Machete®	Monsanto
Magnesium chlorates	Allied, Chevron, Dow, Pennsalt
MCPA	Cleary, Rhodia
MCPA, Potassium salt	Guth
MCPP	Imported
Metobromuron	Imported
MH (maleic hydrazide)	Am. Cy., Ansul, Chem. Form., Fairmont, Uniroyal

TABLE I (Continued)

A. Herbicides and Plant Growth Regulators (Concluded)

Pesticide	Producer
Molinate	Stauffer
Monuron	Du Pont
Monuron-TCA	Allied
Naptalam	Uniroyal
Napthaleneacetic acid and derivatives	Am. Chem., Thom. Hay., Berkeley
Neburon	Imported
Nitralin (Planavin®)	Shell
Nitrofen	Rohm and Haas
Norea	Hercules
Paraquat	Imported
Phosphon®	Mobil
Picloram (Tordon®)	Dow
Preforan®	Geigy
Prometryne	Geigy
Propachlor (Ramrod®)	Monsanto
Propanil	Monsanto, Rohm and Haas
Propazine	Geigy
Propham (IPC)	PPG
Pyrazon	Imported
Siduron	Du Pont
Silvex	Dow, Thom. Hay., Hercules
Simazine	Geigy
Sodium arsenite	Chem Ins., Chev., Chip., FMC, Pennsalt
Sodium borate (metaborate)	U. S. Borax
Sodium chlorate	Am. Potash., Chipman, Hooker, Pennsalt, PPG
2,4,5-T (acid, salts, and esters)	Dow, Thom. Hay.
TCA (sodium salt)	Dow
Terbacil	Du Pont
Terbutol	Hercules
Triallate	Monsanto
Trichlorobenzoic acid, dimethylamine salt	Du Pont
Trifluralin (Treflan®)	Elanco
Vernolate	Stauffer

TABLE I (Continued)

B. Insecticides (including Miticides and Nematocides)

Pesticide	Producer
Abate®	American Cyanide
Acaralate®	Geigy
Aldicarb (Temik®)	Union Carbide
Aldrin	Shell
Aramite®	Uniroyal
Arsenates, calcium and lead	Several Companies
Aspon®	Stauffer
Axinphosmethyl (Guthion®)	Chemagro
Azodrin®	Shell
Bacillus thuringiensis	Abbott, Nutralite, IMC
Baygon® (propoxur)	Imported
Bidrin®	Shell
Binapacryl (Morocide®)	FMC
Bromophos	Imported
2-(p-tert-Butylphenoxy)cyclohexyl-2-propynl sulfite	Uniroyal
Bux Ten®	Chevron
Carbaryl (Sevin®)	Union Carbide
Carbofuran (Furadan®)	FMC
Carbophenothion (Trithion®)	Stauffer
Chlordane	Velsicol
Chlorobenzilate	Geigy
Ciodrin®	Shell
Coumaphos (Co-Ral®)	Chemagro
DDD (TDE)	Allied, Rohm and Haas
DDT	Montrose
Demeton (Systox®)	Chemagro
Diazinon	Geigy
Dichlorvos (DDVP, Vapona®)	Shell
Dicofol (Kelthane)	Rohm and Haas
Dieldrin	Shell
Dilan®	Com. Solv.
Dimethoate	American Cyanide
2,6-Dimethyl-3,5-dichloro-4-pyridinol	Dow
O,O-Dimethyl S-phthalimidomethylphosphorodithioate	Stauffer

TABLE I (Continued)

B. Insecticides (Including Miticides and Nemotocides) (Continued)

Pesticide	Producer
Dioxathion	Hercules
Disulfoton (Disyston®)	Chemagro
Dursban®	Dow
Endosulfan (Thiodan®)	Hooker
Endrin	Velsicol
Ethion	FMC
Fensulfothion (Dasanit®)	Chemagro
Fenthion	Chemagro
Gardona®	Shell
Heptachlor	Velsicol
Isopropylphenyl N-methylcarbamate	Ott
Kepone®	Allied
Lethane 384	Rohm and Haas
Lindane	Hooker
Malathion	American Cyanide
Metaldehyde	Com. Solv.
Methomyl	Du Pont
Methoxychlor	Chem. Form., Du Pont, Nease
Methyl Demeton (Meta Systox®)	Chemagro
Methyl Parathion	Am. Pot., Monsanto, Stauffer, Shell
Mevinphos (Phosdrin®)	Shell
Mirex	American Cyanide
Morestan® (oxythioquinox)	Imported
Naled (Dibrom®)	Chevron
Nemacide (dichlofenthion)	Mobil
Nicotine and derivatives	Chem. Form.
Parathion	Am. Pot., Monsanto, Stauffer, Shell
Perthane®	Rohm and Haas
Petroleum spray oils	Humble, several other companies
N-(Phenyl-2-nitropropyl)piperidine	Merck

TABLE I (Continued)

B. Insecticides (Including Miticides and Nematocides) (Concluded)

Pesticide	Producer
Phorate	American Cyanide
Phosphamidan	Geigy, Mobil
Prophos (Mocap®)	Mobil
Pyrethrum, extract	Imported
Ronnel	Dow
Rotenone, roots	Imported
Ruelene® (Cruformate)	Dow
Sodium fluoride	Allied, Alco, United
Sumithion® (Fenitrothion)	Imported
TEPP	Am. Pot.
Tetradifon	FMC
Thanite	Ott Chemicals
2-Thiocyanoethyl laurate	Rohm and Haas
m-Tolyl-N-methylcarbamate	Ott Chemicals
Trichlorfon	Chemagro
Toxaphene (including strobane-T)	Hercules, Tenneco, Sonford
Zinophos® (Thionazin)	American Cyanide

C. Fungicides

2-Aminobutane Carbonate	Lilly
Benomyl	Du Pont
Bis-1,4-Bromoacetoxy-2-butene	Vineland
2,6-Bis(dimethylaminomethyl)-cyclohexane	Merck
2'-Bromo-4'hydroxacetophenone	Buckman
Cadmium succinate	Mallinckrodt
Captan®	Stauffer
Chloranil	Imported
5-Chloro-2-mercaptobenzothiazole, laurylpyridinium salt	Vanderbilt Chemicals
Chloroneb	Du Pont
Copper carbonate, basic	Mallinckrodt, Tenneco
Copper chloride, basic	FMC, Harshaw

TABLE I (Continued)

C. Fungicides (Continued)

Pesticide	Producer
Copper napthenate	Harshaw
Copper 8-quinolinate	Fisher, Nuodex, Merck
Copper sulfate	Calumet, Harshaw, Phelps Dodge, Tenneco
Cyanodithioimidocarbonate, disodium salt	Buckman
Cyanomethylthiobenzothiazole	Buckman
Dazomet (DMTT)	Merck, Ott, Stauffer, Wood Ridge
DCNA	Upjohn
Dexon®	Imported
Dichlone	Imported
Difolatan (captafol)	Chevron
Dimethyldithiocarbamic acid	
Mn salt	FMC
K salt	Buckman
Dimethylthiocarbonyl	Cleary
Diphenylammonium propionate	Merck
Dodine	American Cyanide
Dyrene®	Chemagro
Ethylene bis(dithiocarbamic acid, diammonium salt)	Roberts
Ferbam	Du Pont, FMC, Vanderbilt, Wood Ridge
Folpet	Stauffer
Glyodin®	Union Carbide
2-Hydroxypropylmethanethio sulfonate	Buckman
Karathane®	Rohm and Haas
Lanstan® (Korax)	FMC
Maneb	Alco, Du Pont, Rohm and Haas
Metham (SMDC)	Stauffer
Mercurial organics (~ 20)	Mallinckrodt, Cleary, Vineland
Mercurial chlorides	Mallinckrodt
2-Mercaptobenzothiazole, zinc and ethanolamine salts	Vanderbilt

TABLE I (Continued)

C. Fungicides (Concluded)

Pesticide	Producer
Nabam	FMC, Rohm and Haas, Uniroyal
PCNB (pentachloronitrobenzene)	Olin
PCP (pentachlorophenol) and sodium salt	Several Companies
Piperalin (Pipron®)	Lilly
Plantvax® (oxycarboxin)	Imported
Polyethylenethiuram disulfide	Buckman
Sulfur and inorganic sulfides	Stauffer, FMC, Olin
2,3,4,6-Tetrachlorophenol	Dow
Thiram	Du Pont
2,4,5-Trichlorophenol	Dow, Hooker, Hercules
Sodium salt	Dow
Ethanolamine salt	GAF
2,4,6-Trichlorophenol	Dow
Zinc sulfate	Several Companies
Zineb	Du Pont, FMC, Rohm and Haas
Ziram	Du Pont

D. Wood Preservatives

Coal tar	Several Companies
Creosote	Several Companies
Acid copper chromate	Several Companies
Chromated copper arsenate	Several Companies
Osmosalts®	Osmose
Tanolith® (Wolman's Salts®)	Koppers
Chromated zinc chloride	Several Companies
PCP (pentachlorophenol and Na salt)	Dow, Monsanto
Petroleum oils	Several Companies

TABLE I (Continued)

E. Fumigants (Soil, Stored Products, Structural, Sterilants)

Pesticide	Producer
Acrylonitrile	Stauffer, Union Carbide, Monsanto, American Cyanide
Azobenzene	Eastern Chemical
Calcium cyanide	American Cyanide
Carbon disulfide	FMC, PPG, Stauffer
Carbon tetrachloride	Dow, Diamond, FMC, Stauffer
Chloroform	Several Companies
Chloropicrin	Dow, IMC
DBCP (dibromochloropropane)	Am. Pot., Dow, Occidental, Shell
D-D®	Dow, Shell
o-Dichlorobenzene	Dow, Monsanto, Hooker
p-Dichlorobenzene	Allied, Monsanto, Dow, PPG
Ethide® (dichloronitroethane)	Com. Solv.
Ethylene dichloride	Five Companies
Ethylene oxide	Dow, Jefferson, Union Carbide, Wyandotte
Ethyl formate	Com. Solv.
Formaldehyde	Allied, Celanese
Hydrogen cyanide	American Cyanide
Methyl bromide	Am. Pot., Dow, Great Lakes, Michigan, Vulcan
Sulfuryl fluoride	Dow

F. Insect Attractants, and Repellants

Deet (diethyltoluamide)	Chem. Form., Hercules, Uniroyal
Ethyl hexandiol (6-12®)	Union Carbide
MGK repellant 326 (di-n-propyl isocinchomeronate)	MGK
Trimedlure	Union Oil Products

TABLE I (Concluded)

G. Synergists

Pesticide	Producer
MGK 264	MGK
Piperonyl butoxide	FMC, Alpha, Berkeley
Tropital®	MGK

H. Rodenticides

Antu®	Penick
Diphacinone	Nease
Norbormide (Raticate®)	Pitman-Moore
Pival® (pindone)	Motomco, Pierce
Sodium fluoroacetate	Roberts Chem.
Strychnine	Imported

I. Miscellaneous Pesticides

Hexachlorophene, a bacteriocide, and fungicide	Imported
3-Trifluoromethyl-4-nitrophenol (TFM), lamphreycide	Maumee
4-Aminopyridine (Avitrol®, bird repellant	Phillips Petroleum Company

J. Dry Carriers and Diluents

Bentonite	Several Companies
Fuller's Earth	Several Companies
Kaolin	Several Companies
Pyrophyllite	Several Companies
Talc and Soapstone	Several Companies

B. Development of Pesticide Use Patterns

The pesticide industry developed as a result of pest control needs in agricultural, structural, home and garden, recreational and other areas. The general classes of pesticides according to the type of pest controlled is shown in Figure 2.

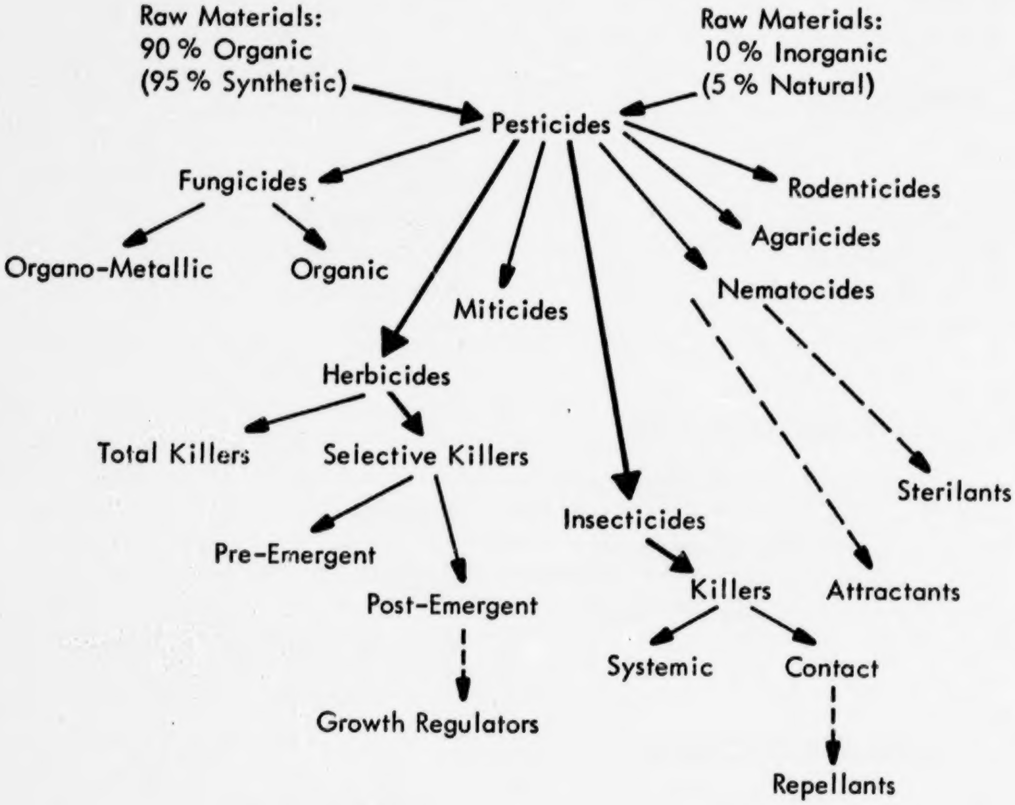

Raw Materials:
90 % Organic
(95 % Synthetic)
Raw Materials:
10 % Inorganic
(5 % Natural)
Pesticides
Fungicides
Organo-Metallic
Organic
Miticides
Herbicides
Total Killers
Selective Killers
Pre-Emergent
Post-Emergent
Growth Regulators
Insecticides
Killers
Systemic
Contact
Repellants
Rodenticides
Agaricides
Nematocides
Sterilants
Attractants

Figure 2 - Classes of Pesticides According to Use[6]

The total use of pesticides has grown rapidly over the past 20 years and the use patterns of pesticides have changed appreciably since these products were first introduced. These changes have not been very drastic from one year to the next, but they have occurred and go on continually, and their accumulative effects are considerable.

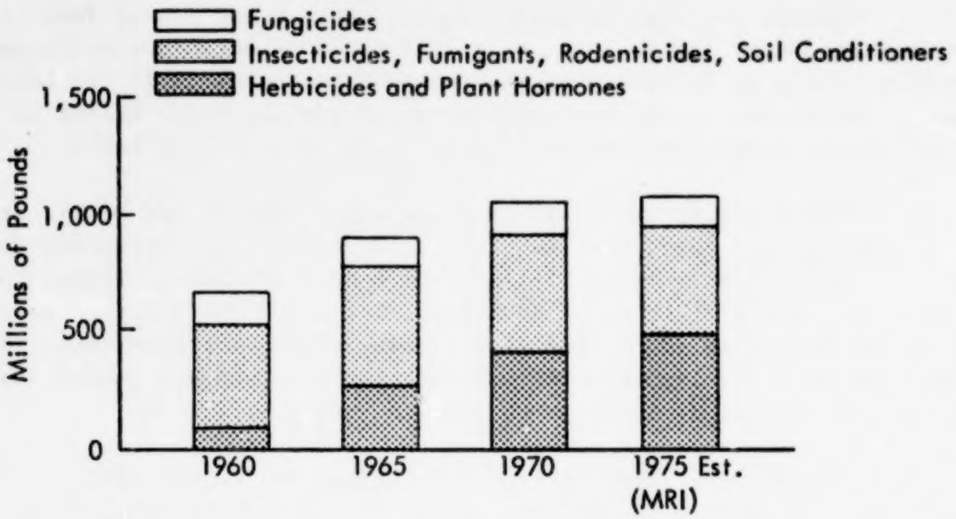
During the last 10 years, the production and use of fungicides has increased very little. The total volume of insecticides has grown somewhat, while by far the greatest increase has occurred in the herbicide field. The growth of the various classes of the pesticide market is illustrated by the production and sales data shown in Figures 3 and 4.

The major agricultural crops of importance to the pesticide market are cotton, corn, soybeans, the various fruit and vegetable crops, hay and pasture, and tobacco, followed by a host of smaller animal and plant uses. The distributions of acreage for major field crops are shown in Figures 5 through 10.[7/] The distribution of use for many nonagricultural pesticides more nearly reflects the population distribution except that usage generally increases as one goes to more southerly latitudes.

The changes which have been occurring in the use patterns of pesticides are significant and are worthy of further comment. These changes are being brought about by several factors, including the following.

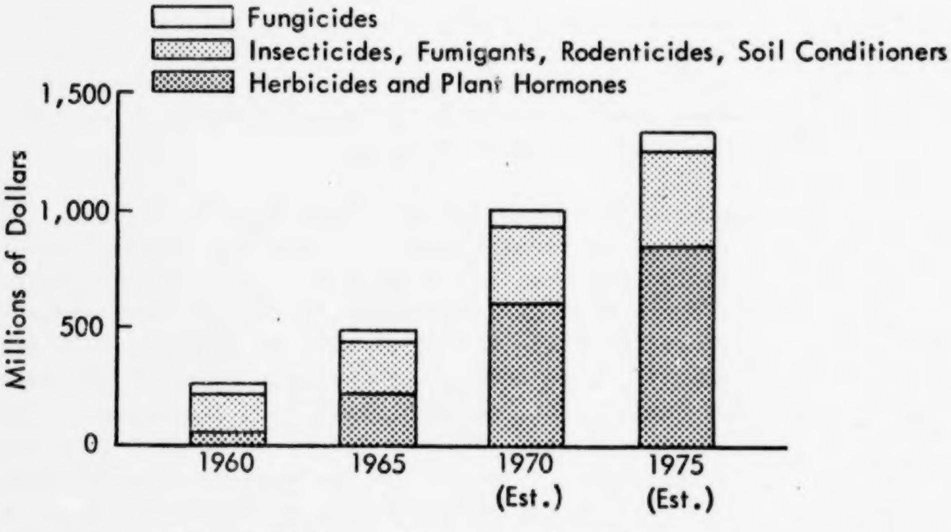
-- Increased general use of pesticides. As the steadily increasing volume of pesticide production and sales indicate, the use of pesticides has increased significantly over the last 10 years. Agricultural uses of pesticides have increased by application of pesticides, especially herbicides, to a larger number of acres. In addition, the rates of application per acre of a number of pesticides, especially insecticides, have increased gradually in response to the development of resistance in the pests to be controlled. Nonagricultural consumption of pesticides has also grown through increased use of pesticides by government agencies, home owners, suburban gardeners, and for a variety of industrial and other purposes.

-- Replacement of pesticides by competitive products. In pest control as in many other fields, the "better" product tends to replace what is only "good." In many instances, more effective or less expensive pesticides have replaced older products in the market place. In general, only pesticides offering more control at the same cost, or the same control at lesser cost, or both, have been successful in replacing other products. Greater safety to humans, to other non-target species, or to the environment have not been equally rewarded in the market place, at least not up to the present time.



Source: U.S. Tarriff Commission (1960 Data Adjusted for Fumigants)

Figure 3 - U.S. Production of Synthetic Organic Pesticides



Adapted from Chemical Week, p. 34, May 27, 1970

Figure 4 - U.S. Producers' Sales of Synthetic Organic Pesticides

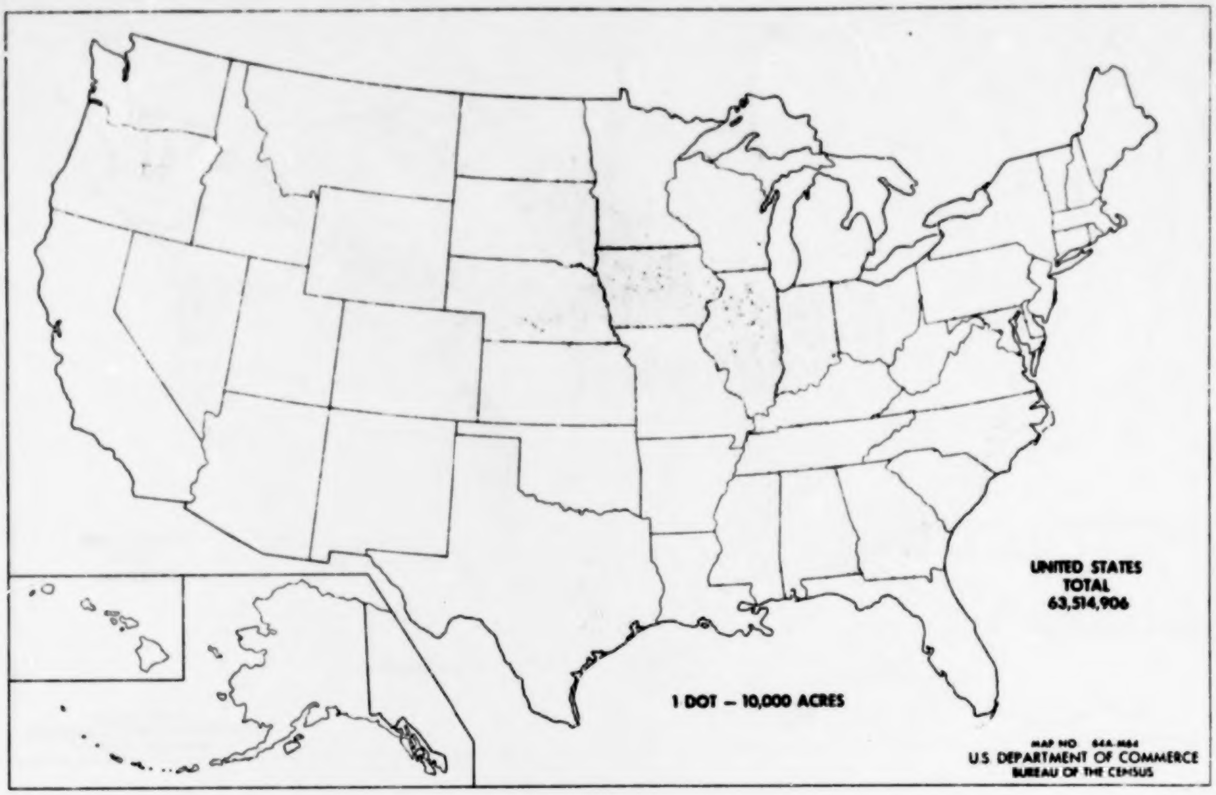

UNITED STATES
TOTAL
63,514,906
1 DOT – 10,000 ACRES
MAP NO 64A-M64
U.S. DEPARTMENT OF COMMERCE
BUREAU OF THE CENSUS

Figure 5 - Corn Harvested for All Purposes, 1964

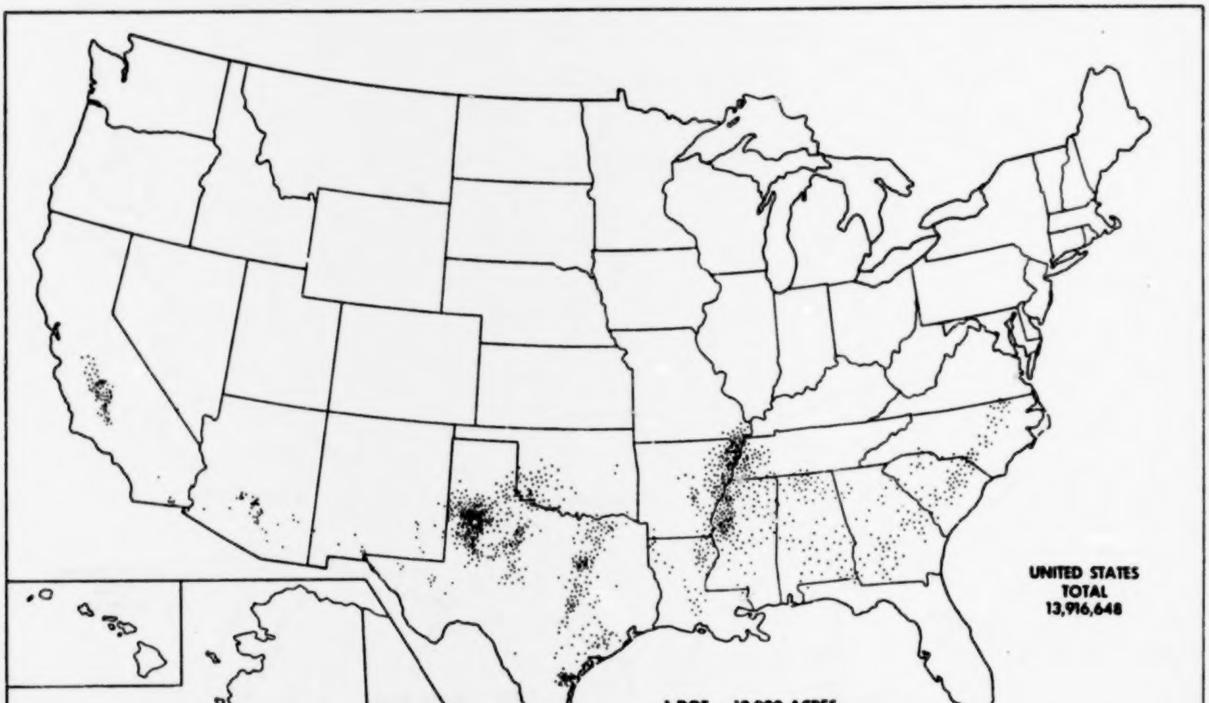

UNITED STATES
TOTAL
13,916,648
1 DOT – 10,000 ACRES
MAP NO 64A-M71
U.S. DEPARTMENT OF COMMERCE
BUREAU OF THE CENSUS

Figure 6 - Cotton Harvested, 1964

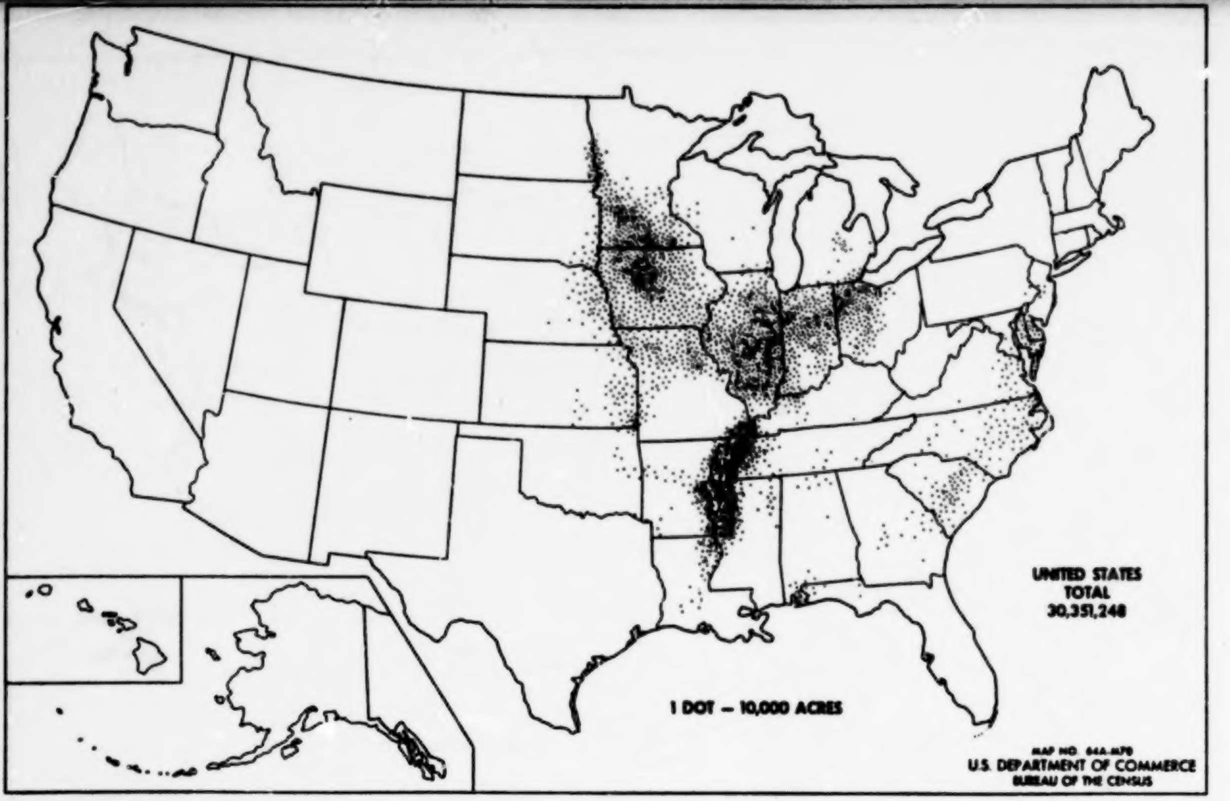

UNITED STATES
TOTAL
30,351,248
1 DOT – 10,000 ACRES
MAP NO. 64A-M70
U.S. DEPARTMENT OF COMMERCE
BUREAU OF THE CENSUS

Figure 7 - Soybeans Harvested for All Purposes, 1964

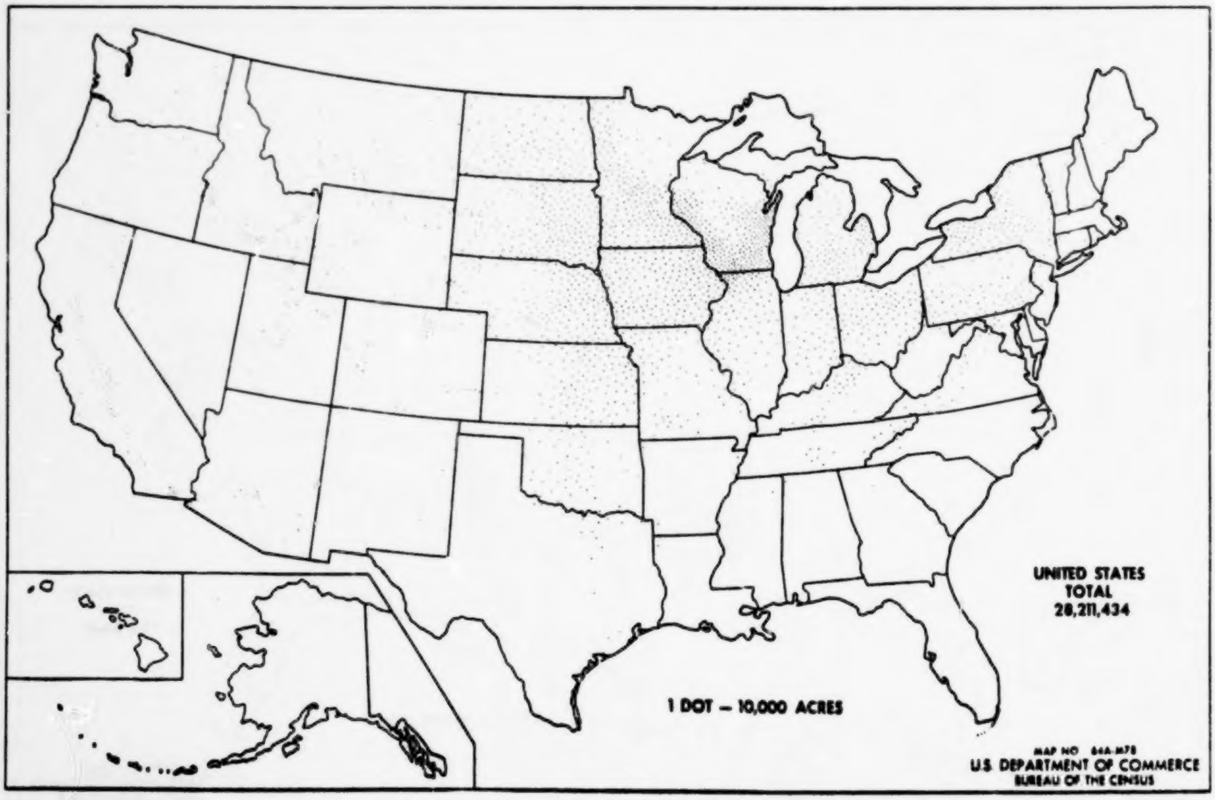

UNITED STATES
TOTAL
28,211,434
1 DOT – 10,000 ACRES
MAP NO. 64A-M78
U.S. DEPARTMENT OF COMMERCE
BUREAU OF THE CENSUS

Figure 8 - Alfalfa Cut For Hay, 1964

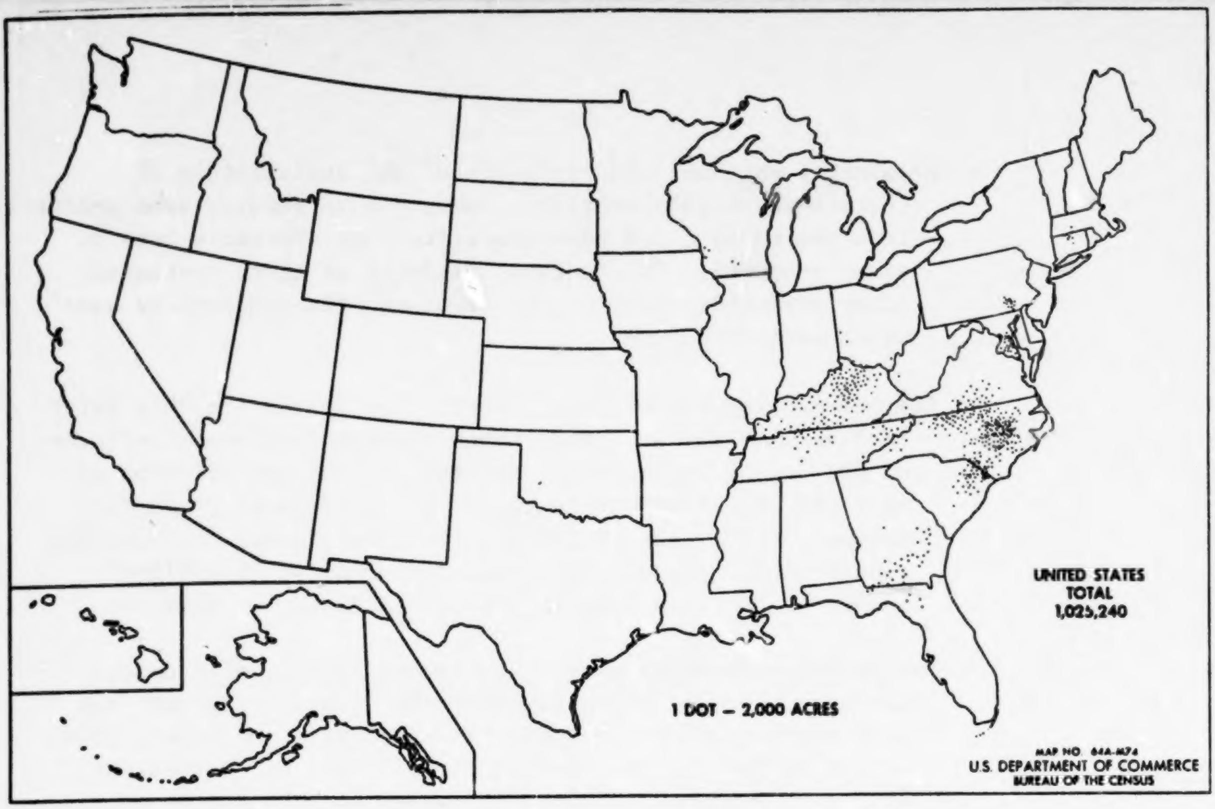

UNITED STATES
TOTAL
1,025,240
1 DOT – 2,000 ACRES
MAP NO. 64A-M74
U.S. DEPARTMENT OF COMMERCE
BUREAU OF THE CENSUS

Figure 9 - Tobacco Harvested, 1964

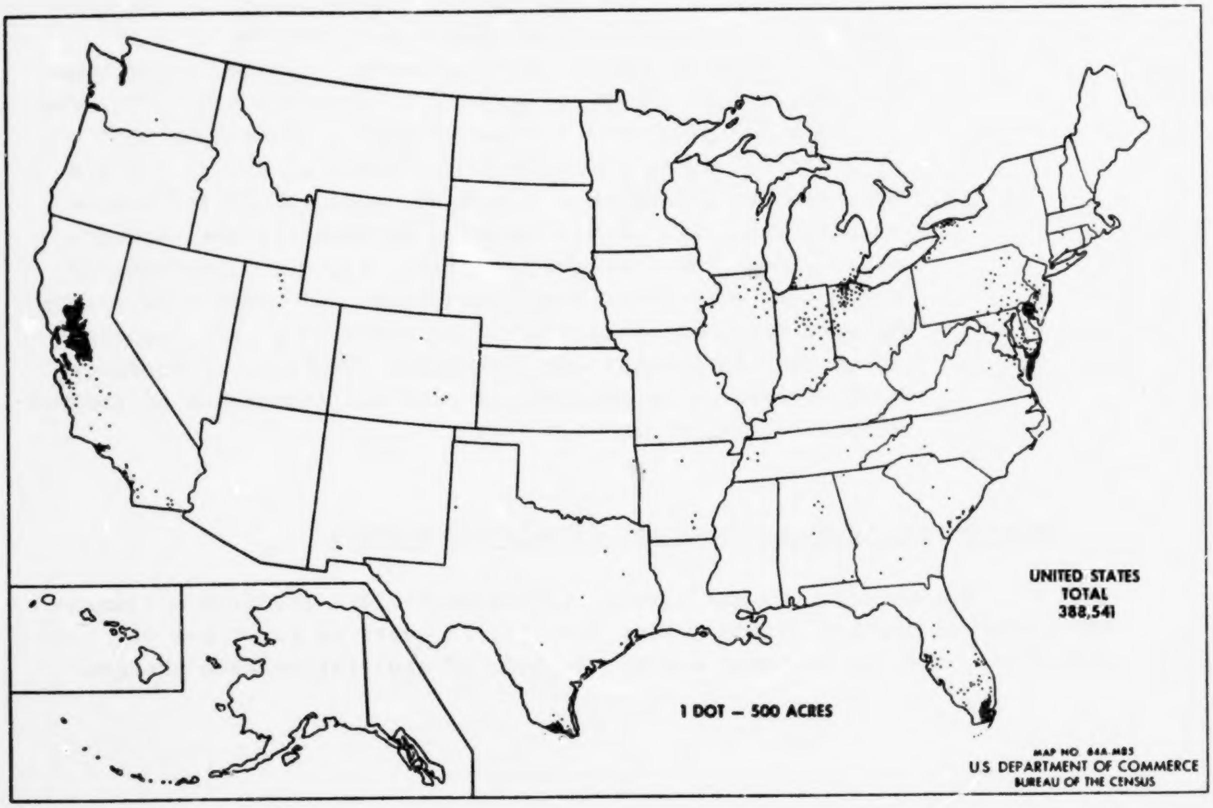

UNITED STATES
TOTAL
388,541
1 DOT – 500 ACRES
MAP NO. 64A-M85
US DEPARTMENT OF COMMERCE
BUREAU OF THE CENSUS

Figure 10 - Tomatoes Harvested For Sale, 1964

-- Regulatory Actions. Cancellation of the registration of certain pesticides or pesticide uses have removed some products from the market, and have restricted the available uses of other products. In the great majority of these instances, other pesticides have quickly replaced the products or uses which were withdrawn.

The chlorinated hydrocarbon insecticides illustrate this point. In line with the worldwide concern about detrimental effects of DDT on the environment, followed by the cancellation of many DDT registrations in the U. S., the annual production volume of this insecticide and its domestic use have dropped considerably. We estimate that "only" about 15 million pounds of DDT were used in the United States in 1971.

The "aldrin-toxaphene group" (including aldrin, chlordane, dieldrin, endrin, heptachlor, Strobane, and toxaphene) has also experienced some decline in production and sales. The use of aldrin for the control of soil insects on corn has decreased somewhat. This is at least in part due to a "secondary" regulatory problem, i.e., widespread appearance of illegal residues of dieldrin, an aldrin metabolite, in food, feed and animal products in areas where aldrin had been in heavy use for many years. (Development of insect resistance has been another factor contributing to the slowly declining use of aldrin on corn.) On the other hand, it appears that larger quantities of products like chlordane and toxaphene are used for many purposes where DDT, aldrin or dieldrin were previously the products of choice. Where chlordane or toxaphene are used as replacements for aldrin or dieldrin, much higher rates of application per acre are usually required. At the same time, analytical methods of sufficient sensitivity and specificity for monitoring chlordane or toxaphene residues in the environment are lacking. It is therefore questionable whether this type of replacement represents an improvement from the standpoint of environmental contamination.

C. Developments in Manufacture and Formulation Methods

The manufacture and formulation of pesticides acquired a tremendous amount of sophistication during the last 25 years as the types of pesticides, the use patterns and the methods of application have changed.

1. Pesticide manufacture: The synthetic chemistry required for the production of the pesticides is generally well known and various aspects are described widely through the technical literature, including the texts, "Organic Insecticides" by Metcalf[4] and "The Chemistry of Pesticides" by Melnikov;[8] certain references such as "Pesticide Manual" by Martin[2] and the "Herbicide Handbook"[9] and special reviews such as that by Riemschneider.[10] The "The Chemical Process Industries" by Shreeve,[11] and "Industrial Chemicals" by Faith, Keyes and Clark[12] describe the production processes for a number of better known pesticides and Sittig's[13] "Pesticide Production Processes" covers the patent literature on the manufacture of about 85 active ingredients. Schematic depictions of the synthesis of some of the more important chemical classes of pesticides are shown in Figures 11 through 15.

The technology for the production of pesticides varies widely depending on the properties of the compounds and the position of the company in terms of raw materials, patent position and sales structure. Production of the early inorganic pesticides was essentially by batch processes and since most of the ingredients were nonvolatile solids or handled in aqueous media, precautions to avoid occupational exposure or environmental pollution were probably minimal. The rise of the petrochemical industry brought an increasing capability to conduct continuous process manufacturing and much of this technology was drawn upon by the synthetic organic pesticide industry, and semicontinuous operations are common. In fact, a number of the petrochemical companies had the raw materials and technical know how to move rapidly into the pesticides field.

The production of synthetic organic pesticides in general, however, involved the use and handling of more hazardous materials (e.g., chloral and chlorobenzene for DDT) than did the inorganics and in many cases the production systems were more carefully controlled or enclosed to avoid occupational exposure. The advent of the chloinesterase-inhibiting organophosphate and carbamate insecticides lead, of necessity, to almost completely enclosed or controlled production systems. While many of the early organic pesticides could be produced with relative ease, many of the highly effective or specific recently developed materials require considerably more sophisticated production chemistry and technology so that the product is quite expensive and more care is exercised to recover the product from waste streams.

In summary, then, one can say that prior to the recently developed consciousness of environmental pollution, the most poorly controlled production processes were those in which the raw materials and product were least toxic to humans and the product could be produced at a low cost. Unfortunately, the persistent DDT fills both of these criteria rather well and one result is that the sediments in the sewer lines below one long-time producer were found to contain 9% DDT--a total of 4,500 lb in 0.5 million pounds of sediment were removed.

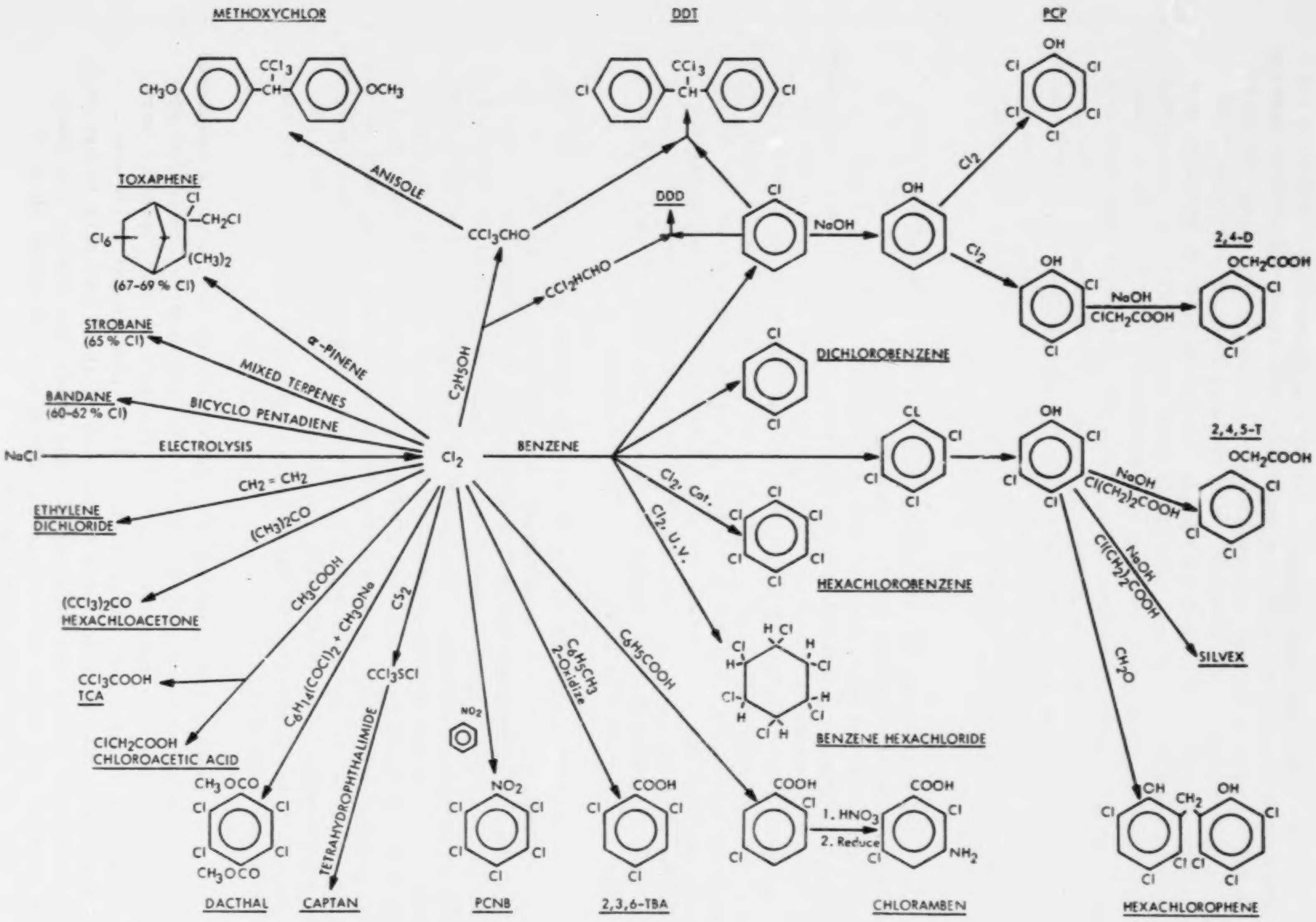

METHOXYCHLOR
DDT
PCP
TOXAPHENE
(67-69 % Cl)
DDD
ANISOLE
CCl3CHO
CCl2HCHO
C2H5OH
NaOH
Cl2
2,4-D
ClCH2COOH
STROBANE
(65 % Cl)
α-PINENE
MIXED TERPENES
BANDANE
(60-62 % Cl)
BICYCLO PENTADIENE
DICHLOROBENZENE
NaCl
ELECTROLYSIS
Cl2
BENZENE
2,4,5-T
CH2 = CH2
ETHYLENE DICHLORIDE
(CH3)2CO
(CCl3)2CO
HEXACHLOACETONE
Cl2, Cat.
Cl2, U.V.
HEXACHLOROBENZENE
Cl(CH2)2COOH
SILVEX
CH2O
CH3COOH
CCl3COOH
TCA
ClCH2COOH
CHLOROACETIC ACID
C6H14(COCl)2 + CH3ONa
CS2
CCl3SCl
TETRAHYDROPHTHALIMIDE
C6H5CH3
2-Oxidize
C6H5COOH
BENZENE HEXACHLORIDE
1. HNO3
2. Reduce
DACTHAL
CAPTAN
PCNB
2,3,6-TBA
CHLORAMBEN
HEXACHLOROPHENE

Figure 11 - Synthesis of Some Chlorinated Hydrocarbons and Related Pesticides

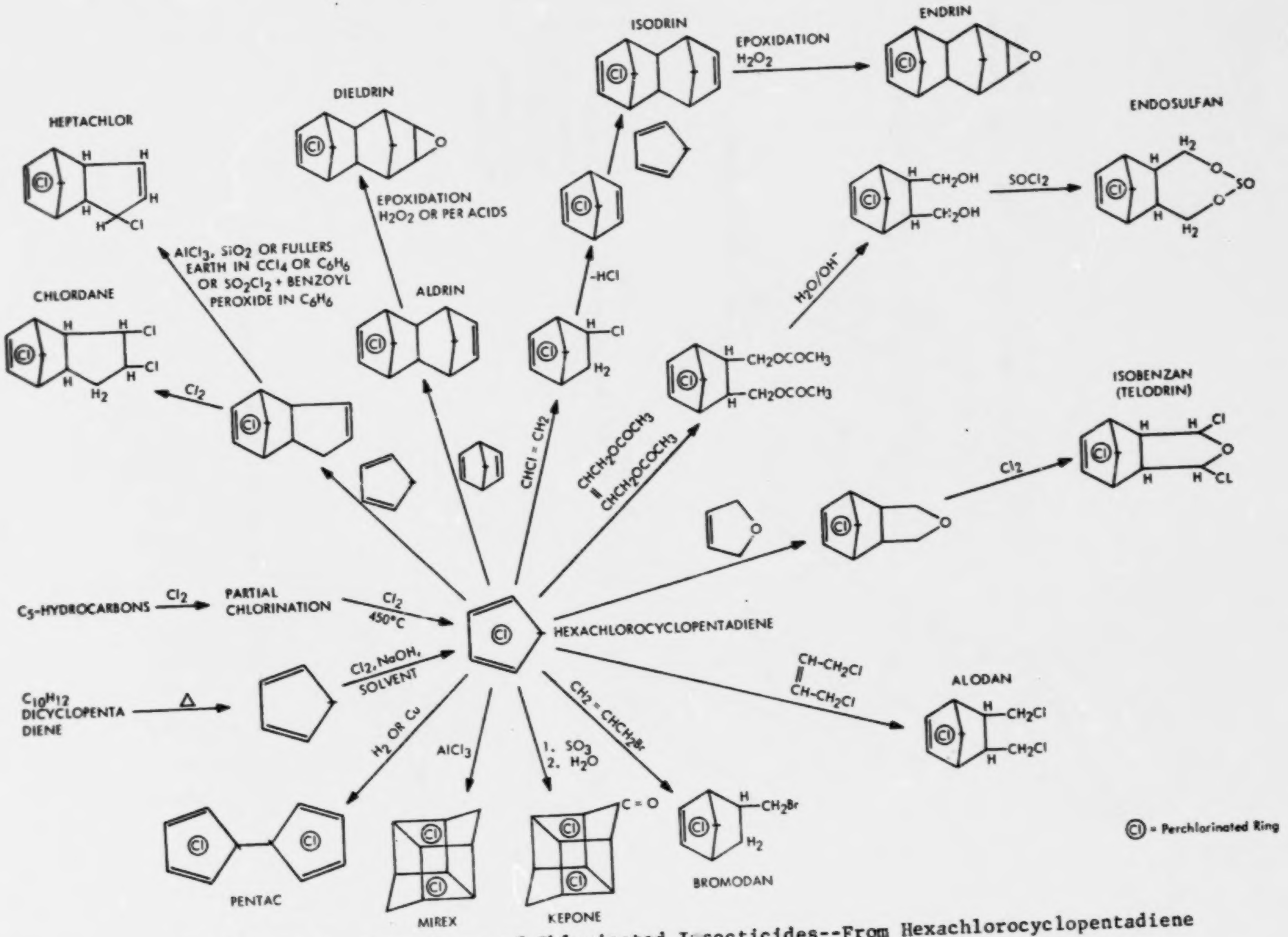

ISODRIN
EPOXIDATION
H_2O_2
ENDRIN
DIELDRIN
ENDOSULFAN
HEPTACHLOR
CH_2OH
CH_2OH
$SOCl_2$
EPOXIDATION
H_2O_2 OR PER ACIDS
-HCl
H_2O/OH^-
$AlCl_3$, SiO_2 OR FULLERS EARTH IN CCl_4 OR C_6H_6 OR SO_2Cl_2 + BENZOYL PEROXIDE IN C_6H_6
CHLORDANE
ALDRIN
CH_2OCOCH_3
CH_2OCOCH_3
ISOBENZAN
(TELODRIN)
Cl_2
$CHCl = CH_2$
$CHCH_2OCOCH_3$
$CHCH_2OCOCH_3$
Cl_2
C_5-HYDROCARBONS
Cl_2
PARTIAL CHLORINATION
Cl_2
450°C
HEXACHLOROCYCLOPENTADIENE
$C_{10}H_{12}$
DICYCLOPENTA DIENE
Δ
Cl_2, NaOH, SOLVENT
CH-CH_2Cl
CH-CH_2Cl
ALODAN
H_2 OR Cu
$AlCl_3$
1. SO_3
2. H_2O
$CH_2 = CHCH_2Br$
C = O
CH_2Br
PENTAC
MIREX
KEPONE
BROMODAN
Cl = Perchlorinated Ring

Figure 12 - Synthesis of the Diene Group of Chlorinated Insecticides--From Hexachlorocyclopentadiene

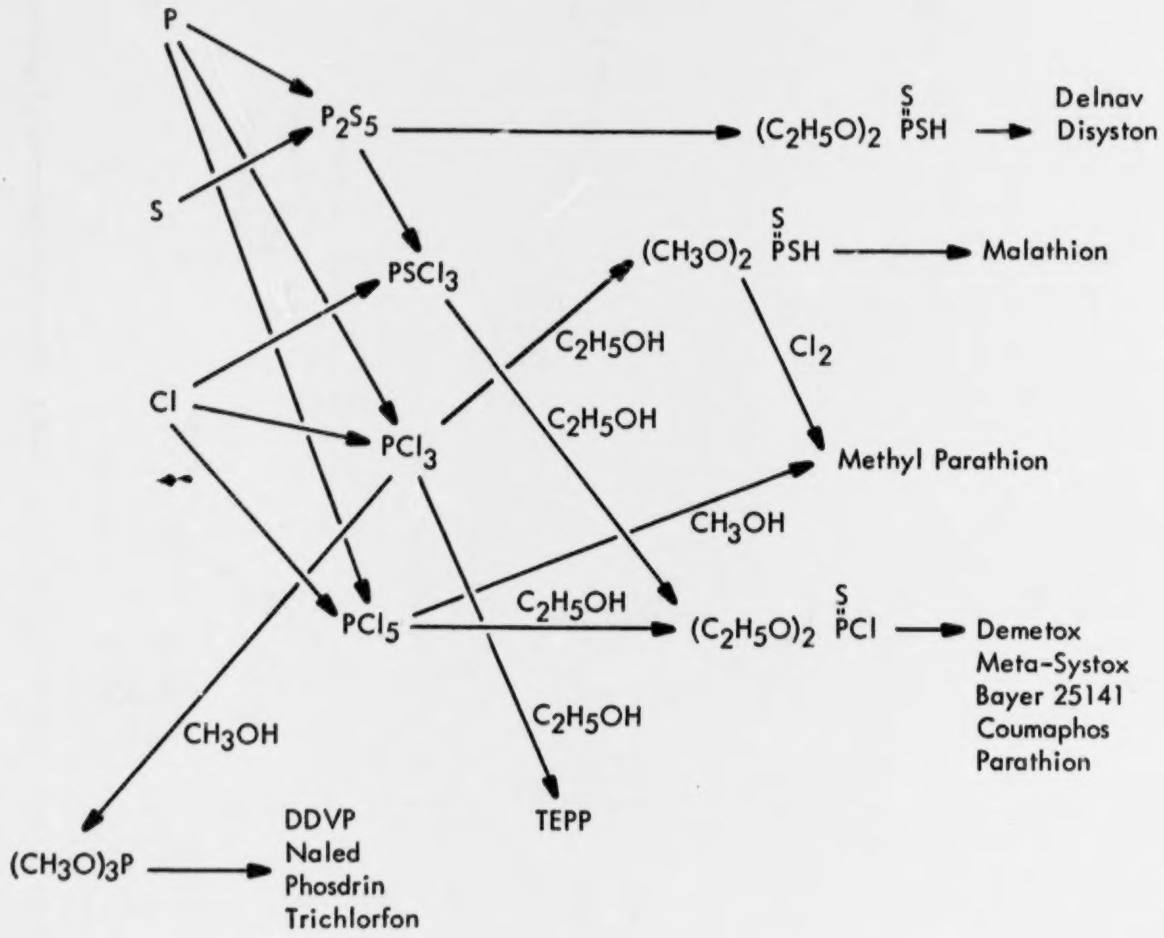
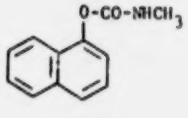

P
P_2S_5
S
$(C_2H_5O)_2\overset{S}{\ddot{P}}SH$
Delnav
Disyston
$PSCl_3$
$(CH_3O)_2\overset{S}{\ddot{P}}SH$
Malathion
C_2H_5OH
Cl_2
Cl
C_2H_5OH
PCl_3
Methyl Parathion
CH_3OH
C_2H_5OH
PCl_5
$(C_2H_5O)_2\overset{S}{\ddot{P}}Cl$
Demetox
Meta-Systox
Bayer 25141
Coumaphos
Parathion
CH_3OH
C_2H_5OH
TEPP
$(CH_3O)_3P$
DDVP
Naled
Phosdrin
Trichlorfon

Figure 13 - Synthesis of Phosphorus-Based Pesticides14/

Reactions **Examples**

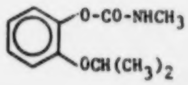
A. **N-Alkyl Carbamates**

1. $ROH(ArOH) + CoCl_2 \xrightarrow{NaOH} ROCOCl \xrightarrow{NH_2R} RO\text{-}CO\text{-}NHR$



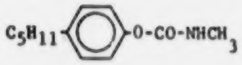
Carbaryl

2. $ArOH + ClCO\text{-}NHR \longrightarrow ArO\text{-}CO\text{-}NHR$

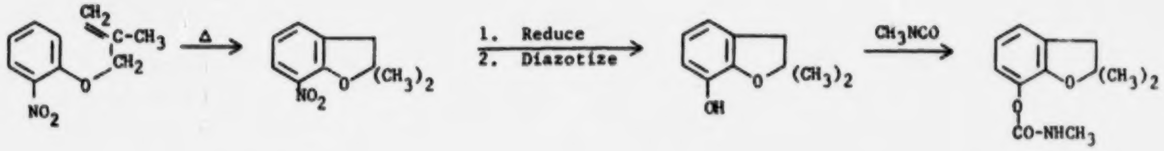

O-CO-NHCH3
OCH(CH3)2

Baygon

3. $ArOH,\ ROH \text{ or } {=}NOH + CH_3NCO \longrightarrow RO\text{-}CO\text{-}NHR$


C5H11
O-CO-NHCH3

Bux


CH2
C-CH3
CH2
O
NO2
Δ
NO2
(CH3)2
1. Reduce
2. Diazotize
OH
(CH3)2
CH3NCO
(CH3)2
O
CO-NHCH3

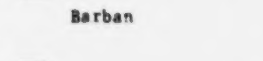
Carbofuran

$(CH_3)_2C{=}CH_2 \xrightarrow[2.\ CH_3SNa]{1.\ NaNO_2 + HCl} CH_3SC(CH_3)_2CH{=}NOH \xrightarrow{CH_3NCO} CH_3SC(CH_3)_2\text{-}CH{=}NO\text{-}CO\text{-}NHCH_3$

Aldicarb

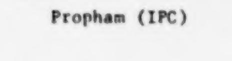
B. **N-Aryl Carbamates**

1. $ArNCO + ROH \longrightarrow Ar\text{-}NH\text{-}CO\text{-}OR$


NH-CO-OCH2C≡CCH2Cl

Barban

2. $ArNH_2 + ClCO\text{-}OR \longrightarrow ArNH\text{-}CO\text{-}OR$


NH-CO-OCH(CH3)2

Propham (IPC)

Figure 14 - Synthesis of Some Carbamate Pesticides

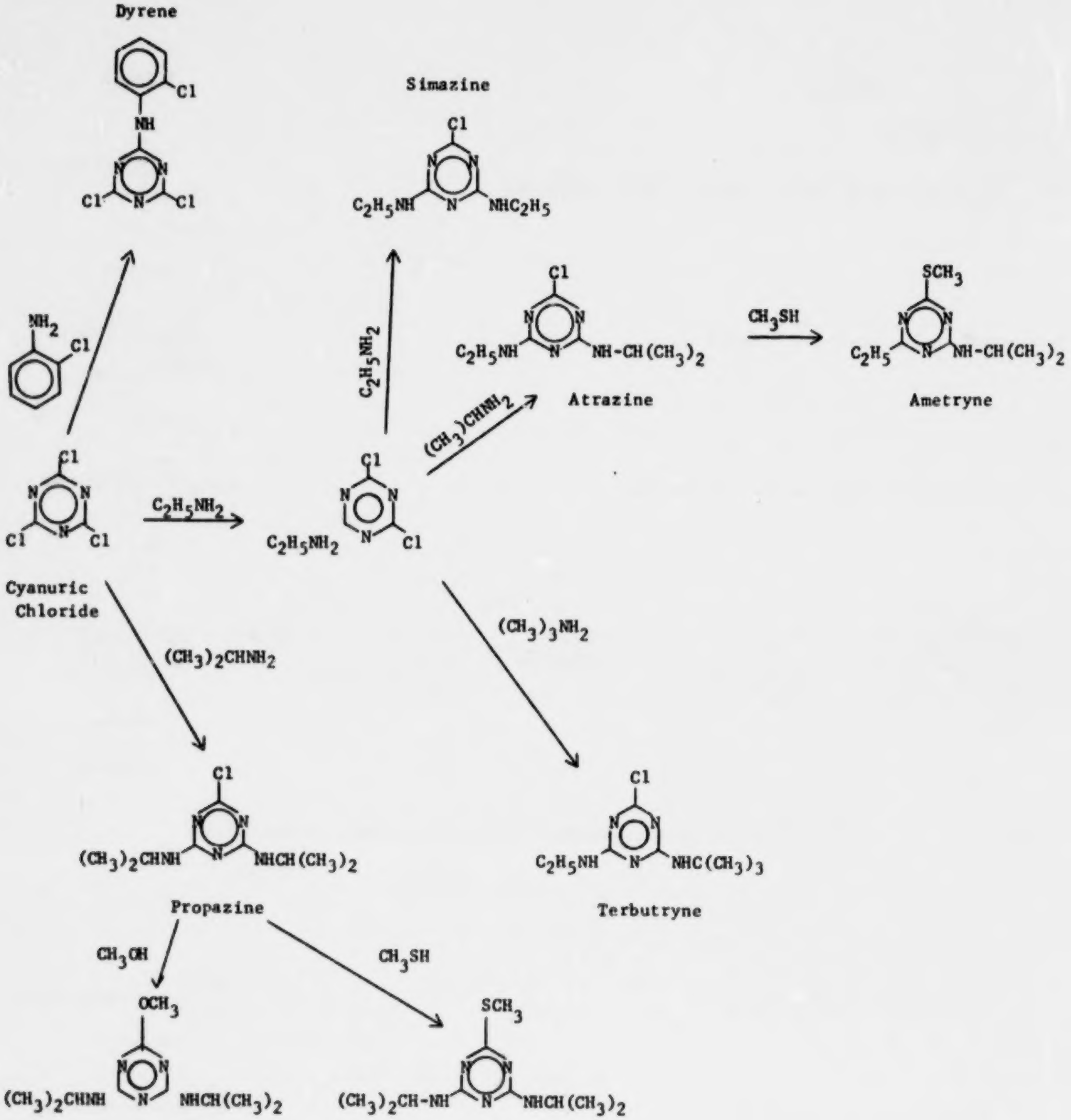

Dyrene
Simazine
Atrazine
Ametryne
Cyanuric Chloride
Propazine
Terbutryne
Prometon
Prometryne
C2H5NH2
C2H5NH2
(CH3)CHNH2
CH3SH
(CH3)3NH2
(CH3)2CHNH2
CH3OH
CH3SH

Figure 15 - Synthesis of Triazine Pesticides

2. Pesticide formulations: The technical product or concentrate produced by the prime manufacturer is usually converted into another form that is both more effectively used as a pesticide and safer for the applicator to use. The effectiveness of a pesticide is dependent upon adequate distribution on the target. Applicator safety is largely dependent on the toxicity of the material being used. These characteristics are obtained by diluting the concentrated pesticide and converting it into a conveniently usable formulation. Dusts, wettable powders, granules, emulsifiable concentrates, and aerosols are the formulations most commonly used. In many cases, two or more active ingredients are used in a formulation to increase its effectiveness and market potential.

The type of formulation manufactured for a specific application is dependent on many factors. Cost and biological efficiency are the most important.[15] Other factors that must be considered are: (1) the biology of the pest and host; (2) the host-pest relationship; (3) the characteristics of available production and application equipment; and (4) the toxicity of the pesticide in relation to plants, animals, and humans.[16] Most agricultural fungicides, for example, are formulated as wettable powders rather than dusts or emulsifiable concentrates. This is true because emulsions are generally more expensive and more difficult to transport, fungicides are less active in the solid than in the liquid state, and because fungicides are often phytotoxic.[15] The solubility characteristics of the pesticide may exclude liquid formulation even where it might be preferred from an application viewpoint. Air milled wettable powers are frequently more expensive than an emulsifiable concentrate.

a. Dusts: Dust is frequently the cheapest and simplest way of applying pesticides.[15] Active ingredient concentrations are generally low, 0.1 to 20%,[17] thus making dust relatively low in toxicity. In recent years, dusts have become less important than the other formulations because of the dependence of dust on climatological factors that cause variable performance as well as drift problems.[18] They were formerly frequently used for soil application and seed treatment.[15]

The physical properties of the dust formulation are largely determined by the properties of the carrier used and the particle size to which it is ground. Some of the more commonly used carriers are organic flours, sulfur, silicon oxides, lime, gypsum, talc, pyrophyllite, bentonites, kaolins, attapulgite, and volcanic ash. Selection of the carrier is critical, and is based on compatibility with the active ingredient, particle size, abrasiveness, density, absorbability, wettability and cost.[17]

In some cases, it is necessary that a stabilizer be added to the dust formulation.[19] Hydrolysis of some organophosphate insecticides in dust formulations, for example, can be inhibited by the use of a stabilizer.

The dust may be formulated by simply mixing or by grinding the ingredients in a hammer, impact, vertical roller, or fluid-energy mill.[15] Another method used is to dilute the active ingredient with a volatile solvent, and then impregnating the carrier with this solution. Some dusts are prepared in two stages.[20] The first stage involves the mixing of the concentrated active ingredient with the carrier to form a dust concentrate, generally containing more than 25% active ingredient.[15] The dust concentrate is convenient to transport and store before being processed into a field strength dust.

b. Wettable powders: Wettable or water-dispersible powders are mixtures of active ingredients, carriers, surface-active agents, and adjuvants that can be suspended in water for application. Wettable powders are formulated with a high active ingredient concentration, usually from 15 to 95%. A surface-active agent is usually added at 1 to 2% to improve the wetting and suspendibility characteristics of the powder. The use of wettable powders has been widely accepted where emulsifiable concentrates are unavailable and because of their greater safety to plants in some instances.[17]

Wettable powders are formulated by processes similar to those used for dust production. The carriers used are similar to those for dust formulations, but are more stringently specified for bulk density and flowability properties.[15]

c. Granules: Granular formulations are generally prepared by the impregnation of the active ingredient on sized granular carriers such as clay, vermiculite, bentonite, or diatomaceous earth.[17,19] The size of the granule normally ranges from 30 to 60 mesh (250 to 590 μ in diameter). Liquid active ingredients can be sprayed directly onto the granular carrier. Solid active ingredients are either melted before being impregnated or applied as slurry.

Granules have advantages in aerial application in that they can penetrate vegetation canopies, they avoid the problem of drift, and control of the rate of toxicant release can often be achieved by changing the ingredients of the formulation. The size of the carrier granule, which can be controlled in the manufacturing process, also influences the redistribution of the active ingredient under the influence of rainfall.[18] This formulation is used primarily for mosquito larvicides and soil applications.[17]

The impregnation is normally accomplished by using ribbon mixers or drum blenders.

d. Emulsifiable concentrates: Emulsifiable concentrates are solutions of active ingredients and surface-active ingredients in water-emulsifiable organic solvents. Active ingredient concentrations generally range from 15 to 50%[17] for single pesticide formulations to as high as about 80% in multiple active ingredient formulations. Surfactants are normally used at a concentration of only a few percent, but are sometimes required in concentrations greater than 5%.[15]

The selection of the solvent to be used is based on many factors, including solvency, specific gravity, flash point, safety to plants and animals, volatility, compatibility, odor, corrosiveness and cost.[17,21] Some of the most commonly used solvents are kerosene, xylenes, methyl isobutyl ketone, and amyl acetate.[17] Xylene, heavy aromatic, and aliphatic type solvents are produced by a number of the major oil companies for use in insecticide formulations.[21]

Emulsifiable concentrates are widely used for household insect control as well as agricultural plant protection. An example of an agricultural concentrate are the three-way blends of toxaphene, DDT, and methyl parathion that were introduced in the late 1950's.[21] These blends, referred to as 4-2-1 or 4-2-1/2, contain 4 lb toxaphene, 2 lb DDT, and 1 or 1/2 lb of methyl parathion per gallon.

e. Aerosols: Aerosol formulations typically contain less than 2% active ingredient in a solvent with small amounts of auxiliary materials. The solvents used include a wide variety of organic materials, such as refined kerosene, and water. Many unusual solvents have been used in specialized aerosols, such as o-dichlorobenzene in garbage can sprays because of its odor-masking characteristic and isoparaffinic-base oil in livestock facefly sprays for safety of the animals mucous membranes.[22]

The auxiliary materials used include a host of special purpose chemicals: Chlorbisan is used in some pet sprays to suppress odor, copper oleate is added to some roach and ant sprays to prevent mildew.[22] A very important category of auxiliary materials is the synergist added to increase the pesticidal properties of the active ingredient. Synergists commonly used include piperonyl butoxide, sulfoxide, and propyl isomer.[22]

The finished aerosol formulations are packaged with a propellant into various types of pressure packs, including true aerosols for space treatment, plant sprays, pet sprays, and repellent sprays for personal use and for use on animals.22/ Propellants used are predominantly mixtures of dichlorodifluoromethane and trichloromethane, although dichlorodifluoromethane is widely used as the sole propellant in pressurized sprays designed to deposit residual insecticides. Methylene chloride, methyl chloroform, N_2O, CO_2, and N_2 are also used to a lesser extent.

Aerosol formulations account for only a small fraction of the active ingredients produced in the United States: 1 to 1.5 million pounds23/ in aerosols versus about 1 billion pounds per year total pesticide production. However, pesticide aerosol accounts for almost 4% of the aerosol containers packaged in the United States (see Figure 43, p. 208).

REFERENCES

1. Frear, D. E. H., The Chemistry of Pesticides (3rd Edition), D. van Nostrand Company, Inc., New York (1955).

2. Martin, H., Pesticide Manual (2nd Edition), British Crop Protection Council, Worchester, England (1971).

3. Jacobson, M., and D. G. Crosby, Naturally Occurring Insecticides, Marcel Dekker, Inc., New York (1971).

4. Metcalf, R. L., Organic Insecticides, Interscience Publishers, New York (1955).

5. Kearney, P. C., and D. D. Kaufman, Degradation of Herbicides, Marcel Dekker, Inc., New York (1969).

6. Report of the Secretary's Commission on Pesticides and Their Relationship to Environmental Health, U. S. Government Printing Office, Washington (1969).

7. "1964 U. S. Census of Agriculture," Vol. III, Part 5, U. S. Department of Commerce, Bureau of the Census, May 1969.

8. Melnikov, N. N., Chemistry of Pesticides, Springer-Verlag, New York (1971).

9. Herbicide Handbook, Weed Science Society of America, Urbana, Illinois (1970).

10. Riemschneider, R., "The Chemistry of the Insecticides of the Diene Group," World Review of Pest Control; Vol. 4, No. 29, pp. 29-61 (1963).

11. Shreve, N., Chemical Process Industries, McGraw-Hill Book Company, New York (1967).

12. Faith, W. L., D. B. Keyes, and R. L. Clark, Industrial Chemicals, (3rd Edition), John Wiley and Sons, Inc., New York (1965).

13. Sittig, M., Pesticide Production Processes, Noyes Development Corp., Park Ridge, New Jersey (1967).

14. Anon., "Pesticides: Present and Future," Chemical Engineering, pp. 133-140, April 7, 1969.

15. Forgeson, D. C., Fungicides, Vol. 1, Academic Press, New York (1967).

16. Coombs, G., "Pesticide Formulation," Agricultural Chemicals, Vol. 15, No. 6, pp. 47-103 (1960).

17. Kirk-Othmer Encyclopedia of Chemical Technology, (2nd Edition), Vol. II, Interscience Publishers, New York, pp. 731-732 (1966).

18. Winchester, J. M., "Future Developments in Pesticide Chemicals and Formulations," Chemistry and Industry, January 27, 1968, pp. 106-108.

19. Anon., "Formulation of Pesticides," Agricultural Chemicals, Vol. 15, No. 3, pp. 35-38 (1960).

20. Personal Communication, Mr. Jack G. Copeland, Hercules, Inc., November 17, 1971.

21. Hersey, J., "Choosing a Solvent for Insecticide Formulations," Farm Chemicals, pp. 42-46, October 1966.

22. Herzka, A., International Encyclopedia of Pressurized Packaging, Pergamon Press, New York (1966).

23. Personal Communication, Mr. Don Gohlson, Cook Chemical Company, November 9, 1971.

III. PRESENT PRODUCTION VOLUMES AND SITES

Nearly 100 companies in the United States are engaged in the production of pesticidal active ingredients and possibly as many as 500 are engaged in the varied aspects of formulating the active ingredients into final products such as liquids, dusts, and packaged aerosol. The total number of formulators and distributors of pesticides is said to be about 1,800 companies. Data on the production volumes of these pesticides and their formulations are almost completely unavailable on an individual compound basis and those which are available leave much to be desired. The basic source of pesticide data for years has been the U.S. Tariff Commission's "Synthetic Organic Chemicals, United States Production and Sales," which contains a two-page tabular summary on "Pesticides and Related Products." This report, issued annually but 2 years after the subject year, is preceded by a preliminary issue of the "Pesticides and Related Products" section of about 10 pages which lists the manufacturing companies who reported production of each synthetic organic pesticidal compound, in addition to the tabular summary. The tabular data are categorized under cyclic and acyclic with subdivisions of (a) fungicides, (b) herbicides and plant hormones, (c) insecticides, rodenticides and fumigants and soil conditions, plus general totals for benzenoid and nonbenzoid chemicals. Thus, the total production of synthetic organic pesticides is listed as 1.03 billion pounds in 1970.[1/]

The major limitation of the tables is that no data on an individual pesticide is published unless three or more manufacturers report, because the data are considered proprietary by the companies and are accepted in confidence by the Tariff Commission. The data are reported for several subcategories such as the aldrin-toxaphene group or the organophosphates, but the "all other" group is invariably so large (e.g., almost two-thirds of the total) as to make meaningful deductions extremely difficult.* In addition, the Tariff Commission data consistently show sales volumes (domestic and exports) of 15-25% less than production volume.

The U.S. Department of Agriculture's Agricultural Stabilization and Conservation Service issues annually[2/] "The Pesticide Review," which tabulates certain data from the Tariff Commission together with supplemental production data on inorganics and organics from the Bureau of Mines and industry sources. It also includes import-export data from the Tariff Commission and Bureau of Census, certain price, transportation and use information, and a brief commentary on aspects and trends in pesticide usage in agriculture. However, little significant new data on production volumes of pesticides are given and, in fact, the USDA's total for "pesticidal chemicals" varies unexpectedly from the Tariff Commission's "synthetic organic pesticides" total: e.g., from 1.5% less than in 1968 to 2.6% more than in 1969.

---

* The situation may be getting worse as the number of producers decrease; for example, DDT now has only one producer and 2,4-D has only two, so that specific production data on these pesticides will become unavailable after 1970.

Certain commercial publications such as Chemical Week and Farm Chemicals also maintain close observation of the pesticide industry and frequently publish reviews and surveys which include forecasts (usually in terms of sales dollars as in Figure 4). Several commercial market survey organizations specialize in collecting this type of information and offer it for sale to their clients. In addition, most if not all of the major pesticide manufacturers have their own market intelligence organizations and systems. Consequently, these groups have their own estimates of the total volume and distribution patterns of pesticides, but this information is closely guarded and generally not accessible to persons outside these organizations. Industry sources have at times revealed certain data, such as that 29 insecticides were produced in amounts of over 1 million pound each in 1968.[3]

Several states have recently started to collect pesticide use data. Among these, California probably has the most complete and advanced system. The California State Department of Agriculture publishes quarterly a "Pesticide Use Report"[4] which details the quantities of pesticides used by product, crop or commodity treated, number of applications of each product on each crop, and individual and total number of acres treated. Similar, but less complete and less sophisticated pesticide use reporting systems were initiated in the five Great Lakes States in 1969, following increasing concern about the contamination of the Great Lakes. The Departments of Agriculture in the states of Illinois,[5] Indiana, Michigan, Minnesota[6] and Wisconsin collect and publish annual information on the farm use of pesticides in each state. However, this information is given in terms of number of acres treated, but not in terms of quantities of specific pesticides applied.

The preceding discussion makes clear that adequate data on the production volumes and the distribution and use patterns of pesticides are not available to the public. Scientists, regulatory officials, legislators, and other members of the public have become increasingly concerned about the unavailability of these data on these and all other hazardous materials. This information is needed for an intelligent assessment of the actual and potential impact of pesticides on the environment, for pinpointing problems requiring research, regulatory or other special attention, for the establishment of meaningful monitoring programs, and for many other purposes. These needs have recently been pointed out emphatically by the "Panel on Monitoring Persistent Pesticides in the Marine Environment" of the Committee on Oceanography, National Academy of Sciences.[7] The Panel recommends that the present legal obstacles to public access to chemical production data be removed, and we concur.

A. Estimated Production of Major Pesticides

In view of the absence of complete and reliable data on pesticide production volumes, intensive efforts were on this program to identify all the major pesticides and to estimate production volumes of all of over 1 million pounds per year. This extensive effort was made to satisfy the specific request of the present contract for "quantitative information on production of major pesticides in recent years," and because of our need for this information in evaluating the pollution potential of the pesticide industry.

The following methods and sources were used in arriving at these estimates. Published data were reviewed in the light of recent changes and trends and our own experience to prepare a tentative list of pesticide production volumes. Subsequently, during our personal interviews with pesticide manufacturers in the field survey phase of this study, we advised each company of our estimates for the production volume of its product(s) and related products and invited comments. The comments were carefully considered, along with many other factors which came to our attention, in our preparation of our "final estimates."

Table II summarizes our estimates of the volume of production for over 150 different pesticides in 1971. Special categories of pesticide data which are provided by the government[1,2] are production of wood preservatives shown in Table III and the import-export figures shown in Tables IV and V, respectively.

Table II does not include every pesticide that the U.S. Tariff Commission[1] says was produced in 1970 (see Table I). Some smaller products have been lumped together in the small remaining "other products" categories under each group of pesticides. Table II does include, we believe, all major pesticides manufactured in the U.S., and most smaller products, including many with a manufacturing volume of less than 1 million pounds per year. This tabulation is the most complete and detailed compilation of the estimated volume of pesticide production which will be available to the public in the United States. We emphasize again that the majority of the production volume figures are our estimates, and that these were arrived at by the use of many different sources of information of varying degrees of reliability. While these estimates lack the authority which could be provided by the Tariff Commission, they are the best available.

TABLE II

ESTIMATED U.S. PESTICIDE PRODUCTION VOLUME, 1971

A. Herbicides (Including Defoliants and Plant Growth Regulators)

Common Name	Trade Name	Principal Manufacturer	Production MM lb A.I.[a]
Atrazine	Aatrex	Ciba-Geigy	90
2,4-D	Several	Several	45
MSMA-DSMA	Several	Several	35
Sodium chlorate	Several	Several	30
Trifluralin	Treflan	Elanco	25
Propachlor	Ramrod	Monsanto	23
Chloramben	Amiben	Amchem	20
Alachlor	Lasso	Monsanto	20
CDAA	Randox	Monsanto	10
Bromacil	Hyvar	Du Pont	8
Nitralin	Planavin	Shell	8
Dicamba	Banvel-D	Velsicol	6
Diuron	Karmex	Du Pont	6
Propanil	Rogue; Stam F34	Monsanto; Rohm & Haas	6
Butylate	Sutan	Stauffer	6
2,4,5-T	Several	Several	6
N.A.	DEF	Chemagro	5
EPTC	Eptam	Stauffer	5
Simazine	Princep	Ciba-Geigy	5
Dalapon	Dowpon	Dow	5
Fluometuron	Cotoran	Ciba-Geigy	4
Propazine	Milogard	Ciba-Geigy	4
Maleic hydrazide	Several	Several	3
Dinoseb	Premerge	Dow	3
Diphenamid	Dymid, Enide	Elanco, Upjohn	3
N.A.	Folex	Mobil	3
Silvex	Several	Several	3
Picloram	Tordon	Dow	3
Cacodylic acid	Several	Ansul	2
Vernolate	Vernam	Stauffer	2

---

[a] MM = million; A.I. = active ingredient.

TABLE II (Continued)

A. Herbicides (Including Defoliants and Plant Growth Regulators) (Concluded)

Common Name	Trade Name	Principal Manufacturer	Production MM lb A.I.
Naptalam	Alanap	Uniroyal	2
Linuron	Lorox	Du Pont	2
Norea	Herban	Hercules	2
TBA	Trysben	Du Pont	2
DCPA	Dacthal	Diamond	2
Endothall	Aquathol	Pennwalt	2
Chlorpropham	Several	PPG	2
Subtotal, 3% herbicides of > 1 MM lb production volume each			408
Acrolein	Aqualin	Shell	< 1
N.A.	Ammate	Du Pont	< 1
Amitrole	Several	American Cyanamid	< 1
N.A.	Bandane	Velsicol	< 1
Barban	Carbyne	Gulf	< 1
Benefin	Balan	Elanco	< 1
Bensulide	Betasan, Prefar	Stauffer	< 1
CDEC	Vegadex	Monsanto	< 1
Chlorbromuron	Maloran	Ciba-Geigy	< 1
Chlorboxuron	Tenoran	Ciba-Geigy	< 1
Cycloate	RoNeet	Stauffer	< 1
Diallate	Avadex	Monsanto	< 1
Fenuron	Dybar	Du Pont	< 1
Fluorodifen	Preforan	Ciba-Geigy	< 1
Molinate	Ordram	Stauffer	< 1
Monuron	Telvar	Du Pont	< 1
Pebulate	Tillam	Stauffer	< 1
Siduron	Tupersan	Du Pont	< 1
Terbacil	Sinbar	Du Pont	< 1
Terbutol	Azak	Hercules	< 1
TCA	Several	Dow	< 1
Triallate	Avadex BW, Far-Go	Monsanto	< 1
Subtotal, 22 listed herbicides of < 1 MM lb production volume each			15
All other herbicides			5
Total, All Herbicides			428

TABLE II (Continued)

B. Synthetic Organic Insecticides, Miticides, Nematocides

Common Name	Trade Name	Chemical Group[a]	Principal Manufacturer	Production MM lb A.I.
Toxaphene	Several (incl. Strobane-T)	CH	Hercules, Tenneco	50
DDT	Several	CH	Montrose	45
Carbaryl	Sevin	CA	Union Carbide	45
Methyl parathion	Several	OP	Monsanto	45
Malathion	Cythion	OP	American Cyanamid	35
Chlordane	Several	CH	Velsicol	25
Parathion	Several	OP	Monsanto	15
Aldrin	Several	CH	Shell	10
Methoxychlor	Several	CH	Du Pont	10
Diazinon	Spectracide	OP	Ciba-Geigy	10
Carbofuran	Furadan	CA	FMC	8
Disulfoton	Di-Syston	OP	Chemagro	8
Phorate	Thimet	OP	American Cyanamid	8
Heptachlor	Several	CH	Velsicol	6
N.A.	Bux	CA	Ortho	6
N.A.	Dursban	OP	Dow	5
Dicofol	Kelthane	CH	Rohm & Haas	4
Azinphos-methyl	Guthion	OP	Chemagro	4
Fensulfothion	Dasanit	OP	Chemagro	4
Methomyl	Lannate	CA	Du Pont	3
N.A.	Dyfonate	OP	Stauffer	3
Ethion	Nialate	OP	FMC	3
Ronnel	Korlan	OP	Dow	3
Carbophenothion	Trithion	OP	Stauffer	2
Naled	Dibrom	OP	Ortho	2
Dimethoate	Cygon	OP	American Cyanamid	2
Aldicarb	Temik	CA	Union Carbide	2
Endosulfan	Thiodan	CH	FMC	2
Chlorobenzilate	Several	CH	Ciba-Geigy	2
Crufomate	Ruelene	OP	Dow	2
Subtotal, 30 insecticides of > 1 MM lb production volume each				368

---

[a] CH = chlorinated hydrocarbon.
OP = organophosphate.
CA = carbamante.

TABLE II (Continued)

B. Synthetic Organic Insecticides, Miticides, Nematocides (Concluded)

Common Name	Trade Name	Chemical Group[a]	Principal Manufacturer	Production MM lb A.I.
N.A.	Abate	OP	American Cyanamid	< 1
Coumaphos	Co-Ral	OP	Chemagro	< 1
Fenthion	Baytex	OP	Chemagro	< 1
Dioxathion	Delnav	OP	Hercules	< 1
Dichlofenthion	VC-13	OP	Mobil	< 1
Thionazin	Zinophos	OP	American Cyanamid	< 1
Dichlorvos	DDVP	OP	American Cyanamid	< 1
Oxydemeton-me	Meta-Systox-R	OP	Chemagro	< 1
Mevinphos	Phosdrin	OP	Shell	< 1
Phosphamidon	Dimecron	OP	Ciba-Geigy	< 1
Dicrotophos	Bidrin	OP	Shell	< 1
Monocrotophos	Azodrin	OP	Shell	< 1
N.A.	Aspon	OP	Stauffer	< 1
TEPP	Several	OP	Several	< 1
N.A.	Mocap	OP	Mobil	< 1
Dieldrin	Several	CH	Shell	< 1
Endrin	Several	CH	Shell	< 1
Lindane	Several	CH	Hooker	< 1
N.A.	Mirex	CH	Allied Chemical	
Chloropropylate	Acaralate	CH	Ciba-Geigy	< 1
N.A.	Omite	MI	Uniroyal	< 1
Binapacryl	Morocide	MI	FMC	< 1
Subtotal, 21 listed insecticides of < 1 MM lb production volume each				15
All other synthetic organic insecticides, miticides, nematocides				10
Total, All Synthetic Organic Insecticides, Miticides, Nematocides				393

TABLE II (Continued)

C. Botanical, Biological, and Inorganic Insecticides; Attractants, Repellents and Synergists

Common Name	Trade Name	Type Product	Principal Manufacturer	Production MM lb A.I.
Botanical and Biological Insecticides				
Bacillus thuring.	Dipel		Abbott, Nutrilite	1
Polyhedr. virus	Viron H		IMC	< 1
Pyrethrins	Several		FMC, MGK	< 1
Rotenone	Several		Several	< 1
Nicotine	Black Leaf		Chem. Form.	< 1
Inorganic Insecticides				
Pb-arsenate	Several		Several	6
Ca-arsenate	Several		Several	2
Attractants, Repellents, Synergists				
DEET	Several	Rep.	Several	1
Piperonyl butoxide	Several	Syn.	FMC	1
Ethyl hexandiol	6-12	Rep.	Union Carbide	< 1
N.A.	MGK-326	Rep.	MGK	< 1
Trimedlure	N.A.	Att.	Universal Oil	< 1
N.A.	MGK-264	Syn.	MGK	< 1
Heliotropin acetal	Tropital	Syn.	MGK	< 1
Other Attractants, Repellents, Synergists				< 1
Total, All Products				13
Special Category				
Petroleum oils including synthetic spray oils, deodorized kerosene, and other petroleum distillates used as diluents and carriers				a/

---

a/ No date available; possibly 1 billion pounds or more.

TABLE II (Continued)

D. Fungicides

Common Name	Trade Name	Principal Manufacturer	Production MM lb A.I.
PCP and salts	Several	Several	46[a]
Dithio-carbamates	Several	Several	40[b]
TCP and salts	Several	Dow	20
Captan	Orthocide	Stauffer	18
PCNB	Several	Olin	3
Dodine	Cyprex	American Cyanamid	3
Captafol	Difolatan	Ortho	2
Folpet	Phaltan	Stauffer	2
Cu-naphtenates	Several	Several	2
Subtotal, 9 listed fungicides >1 MM lb production volume each			136
Aminobutane	Several	Elanco	<1
Benomyl	Benlate	DuPont	<1
Chloroneb	Demosan	DuPont	<1
DCNA	Botran	Upjohn	<1
Dinocap	Karathane	Rohm & Haas	<1
DMTT	Dazomet, Mylone	Several	<1
Glyodin	Glyodin	Union Carbide	<1
Tetra-CP	Several	Dow	<1
Hg-salts	Several	Mallinckrodt	<1
Subtotal, 9 listed fungicides <1 MM lb production volume each			7
All other synthetic organic fungicides			2
Total, all Above Products			145
Inorganic Sulfur and Sulfides			150
Inorganic Copper Salts			2[c]
Total, all Fungicides			297

---

[a] Includes use as herbicide, desiccant, molluscicide and for termite control (see Table III).

[b] Includes CDEC, Dithane M-45®, Dithane S-31®, Ferbam, Maneb, Metham, Nabam, Niacide®, Polyram®, Thiram, Zineb and Ziram.

[c] Published data are extremely unreliable, e.g., 45 MM lb in Ref. 2.

TABLE 11 (Concluded)

E. Rodenticides, Molluscicides, Fumigants, Soil Conditioners, etc.

Common Name	Trade Name	Principal Manufacturer	Production MM lb A.I.
Rodenticides			
Warfarin	Several	Several	12
Dipacinone	Diphacin	Nease	<1
Norbormide	Raticate	Pitman-Moore	<1
Pindone	Pival	Several	<1
ANTU	Several	Penick	<1
Na-fluoracetate	Several	Aceto	<1
Molluscicides			
Metaldehyde	Several	Comm. Solvents	<1
Fumigants (Soil, Stored Product, Structural, and Household)			
Methyl bromide	Several	Several	22
DBCP	Several	Several	10
Other acyclic organics			
dichloro-propene-propane mixtures	D-D, Nemex, Vidden D, Telone	Dow, Shell	75[a]
carbon disulfide	Several	Several	
carbon tetrachloride			
ethylene dichloride-dibromide			
chloropicrin			
formaldehyde			
and others			
Dichlorobenzene	Several	Several	60[b]
Napthalene	Several	Several	2[a]
Inorganic fumigants	Several	Several	5
Soil Conditioners			
Polyacrylonitrile	N.A.	American Cyanamid	10
Other soil conditioners			
Total, all Rodenticides, Molluscicides, Fumigants, Soil Conditions, etc.			200

---

[a] Excludes nonfumigant use.

[b] Includes moth-proofing and lavatory-space deodorant use.

TABLE III

UNITED STATES USAGE OF WOOD PRESERVATIVES, 1965-69[2]

Kind of Preservative	1967	1968	1969
		Liquids	
	1,000 gal.	1,000 gal.	1,000 gal.
Creosote	147,594	136,799	128,226[a]
Petroleum	73,661	73,588	68,071
Coal tar	20,082	20,469	19,618
Total	241,337	230,856	215,915
		Solids	
	1,000 lb	1,000 lb	1,000 lb
Pentachlorophenol	24,814	26,389	25,542
Tanalith®[b] (Wolman Salts®)	3,922	2,683	3,067
Chromated zinc chloride[c,d]	1,664	1,526	1,384
Acid copper chromate	1,405	1,139	872
Osmosalts®[e]	1,419	1,288	1,472
Chromated copper arsenate[c,f]	2,330	3,215	4,668
Other	1,281	1,554	1,050
Total	36,835	37,794	38,055

---

[a] Estimate 1 billion pounds, 1971.

[b] Mixture of Na_2CrO_4 (37.5%), NaF (25%), Na_2HAsO_6 (25%) and Dimitrophenol (12.5%).

[c] Includes copperized.

[d] Includes fire retardant use.

[e] Apparently similar to Tanalith.

[f] Includes Boliden Salts® which contain arsenic, chromium, and zinc.

TABLE IV

UNITED STATES IMPORTS OF SYNTHETIC ORGANIC PESTICIDES, 1965-69[c]

Pesticide[a]	1967 (lb)	1968 (lb)	1969 (lb)
		Fungicides	
Chloranil	130,870	103,410	110,109
Copper 8-quinolinolate	47,600	7,071	1,000
Dexon®	14,062	31,923	11,243
Dichlone	36,574	172,758	148,079
Oxycarboxin (Plantvax®)	0	0	10,250
Pentachloronitrobenzene	30,000	20,000	132,400
Thiram	110,538	107,001	0
2,4,5-Trichlorophenol	71,0[illegible]0	79,261	0
		Herbicides	
Bromoxynil	58,000	40,240	65,280
Chloroxuron	165,380	145,502	0
Dichlobenil	0	0	34,888
2,4-D	2,805,354	2,473,578	0
Dinitrocresol	42,952	55,040	6,400
Dichlorprop	604,160	535,563	525
Diquat dibromide	107,670	374,100	744,318
Ioxynil	0	3,300	0
Maleic hydrazide	0	0	3,307
MCPA	141,736	0	104,107
MCPB	40,318	39,352	0
Mecoprop	120,406	136,055	312,627
Neburon	40,000	64,092	60,036
Nitrofen	0	22,046	0
Paraquat[b]	1,033,525	1,663,683	2,945,619
Phenmedipham (Betanol®)	0	0	48,505
Metobromuron	110	24,967	49,714
Preforan®	0	0	82,407
Pyrazon	111,039	144,472	103,040
2,4,5-T	25,904	315,556	45,418
		Insecticides and Miticides	
Aldrin	212,082	0	0
Propoxur (Baygon®)	33,069	172,777	83,100
Bromophos	0	0	199,956
Dicofol	0	0	4,564
Dieldrin	0	0	12,885
Lindane	0	0	0
Malathion	0	551	466,291
Methyl parathion	126,765	0	0
Oxythioquinox (Morestan®)	0	0	40,265
Parathion	20,944	0	0
Piperonyl butoxide	11,464	0	0
Fenitrothion (Sumithion®)	4,409	0	11,022
Zinophos	31,416	0	0
		Rodenticides	
ANTU	2,000	3,637	5,676
Pindone	0	210	0
Warfarin	11,308	1,241	10,420
		Other	
p-Chloro-m-cresol	42,519	72,508	28,347
Hexachlorophene	88,184	0	150,321

---

[a] Minor items not shown.

[b] Includes dichloride and bis(methyl sulfate).

[c] MRI estimate for 1971: 1 million pounds.

TABLE V

UNITED STATES EXPORTS OF PESTICIDES, 1968-69[2]

Export Grouping	Volume 1968 1,000 lb	 1969 1,000 lb
	Fungicides	
Inorganic fungicides, tech[a]	1,855.0	6,255.9
Organic fungicides, tech	5,480.2	5,017.7
Fungicide formulations[b]	30,294.2	24,974.1
Total	37,629.4	36,247.7
	Herbicides	
Inorganic herbicides, tech[c]	2,325.3	2,870.4
2,4-D and 2,4,5-T tech. acid basis[d]	3,391.0	7,287.1
Other organic herbicides, tech	20,822.1	27,564.5
Herbicide formulations[e]	46,326.8	31,759.7
Total	72,865.2	69,481.7
	Insecticides	
Inorganic insecticides, tech[f]	2,276.8	5,466.7
DDT, tech	38,998.0	27,900.7
DDT, 20-74%, 100% basis	6,923.8	5,554.8
DDT, 75%, plus, 100% basis	63,226.4	48,621.5
Other polychlor insecticides, tech[g]	67,532.8	30,198.6
Other polychlor formulations	8,683.5	14,697.8
Organic phosphorus insecticides, tech	56,146.8	57,157.0
Organic phosphorus formulations	7,672.4	7,738.4
Other organic insecticides, tech	29,821.2	25,615.6
Other organic formulations	32,489.5	17,068.9
Household and industrial formulations[h]	8,752.1	10,519.5
Total	322,523.3	250,539.5
	Other	
Organic rodenticides, tech	604.5	396.1
Disinfectants, tech	4,077.2	3,819.7
Disinfectant formulations	6,046.5	5,956.0
Dips, growth regulators	3,959.4	5,669.0
Organic fumigants	24,106.1	37,274.0
Total	38,793.7	53,114.8
Grand Total	471,811.6	409,383.7

---

a/ Includes copper sulfate, sulfur, etc.; see next footnote.

b/ Includes conditioned sulfur dust and sulfur pastes, precipitated, colloidal, and flowers of sulfur are not shown.

c/ Includes sodium arsenite.

d/ Includes technical salts and esters on acid basis.

e/ Includes calcium cyanamide for weed control and defoliation.

f/ Includes calcium arsenate and lead arsenate; also inorganic fumigants and rodenticides.

g/ Includes technical BHC and paradichlorobenzene.

h/ Includes repellents and rodenticide preparations.

The production data shown in Tables II and III show that the pesticide market is dominated by a small number of major products, while a large number of minor products compete for a small share of the market. By far the largest pesticidal class of ingredients used is the petroleum oils of all types, including the synthetic and refined oils used as insecticidal spray oils, the diluent and carrier oils used for thousands of formulations, and the 0.5 billion pounds per year used as wood preservative. The next largest product is the general purpose wood preservative, creosote, for which production is about 1 billion pounds per year. However these products, along with the 160 million pounds per year of coal tar and other products, used as wood preservatives do not appear to be of major concern as environmental pollutants (although more study of their effects is obviously needed) and will not be considered further here.

Based on the data in Table II the total pesticide production in the United States is about 1.344 billion pounds per year, excluding the petroleum and coal products. Of the synthetic organics, six products are produced in amounts of 45 million pounds per year or more. These are: the agricultural herbicide atrazine; the insecticides DDT; toxaphene, carbaryl and methyl parathion; the herbicide 2,4-D used agriculturally, on rights of way, etc.; and the wood preservative and herbicide pentachlorophenol. (Dichlorobenzene also falls in this production category, but the use breakdown between moth control and lavatory-space deodorant is uncertain.) These six products account for over 25% of the total volume of pesticide production.

Nine herbicidal products are produced in amounts of over 10 million pounds per year and have a combined total production of 298 million pounds per year. Ten insecticides are in the 10 million pounds per year class and account for 290 million pounds per year. Five fungicides or classes of fungicides (inorganic sulfides, pentachlorophenol and salts, trichlorophenol and salts, the dithiocarbamate group, and captan) are over the 10 million pounds per year mark and account for a total of 274 million pounds per year. These 24 product groups have a combined production volume of 862 million pounds per year or about 64% of the total for all pesticides.

The remaining 26% of production is divided between about 250 other pesticides, of which 133 are listed in Table II. Some 65 to 75 of these are estimated to have production volumes of over 1 million pounds per year each, and about 60 are produced in less than 1 million pounds per year quantities but are sufficiently important that they were included in Table II.

A further summary of the major herbicides, insecticides and fungicides is given in Table IV. For the 135 specified products or groups of products the average production volume is 7.4 million pounds per year and is about the same for all three classes.

Further information and comment on the production and use of 22 major pesticides are given in Chapter IV.

TABLE VI

SUMMARY OF PRODUCTION VOLUMES OF SELECTED HERBICIDES, INSECTICIDES, AND FUNGICIDES

Pesticide Group	Number of Products by Production Volume Ranges (MM lb)						Total No. of Specified Products	Production Volume (MM lb)		
	> 45	< 45-25	< 25-10	< 10-5	< 5-1	< 1		Specified Products	Unspecified Products	All Products
Herbicides[a/]	1	4	4	11	17	22	59	423	5	428
Insecticides[b/]	3	3	4	6	15	25	58	393	10	403
Fungicides[c/]	0	2	2	0	5	9	18	143	2	145
Total	4	11	10	17	37	56	135	959	17	976

---

a/ Including defoliants and plant growth regulators.

b/ Including organic, inorganic, and biological insecticides; excluding attractants, repellents, synergists; rodenticides, molluscicides, fumigants, and soil conditioners.

c/ Considering the dithiocarbamate as a single product, and counting pentachlorophenol as primarily a fungicide, but excluding sulfur, inorganic Cu and other salts.

B. Geographical Location of Producers and Transportation Patterns

The location of the production sites for pesticides is to a considerable degree influenced by the proximity to raw materials and to major use areas for specific products, and also by the existing plant facilities which a company has when production of a new product is being planned. Thus, the production sites are clustered in several centers including: the New York-New Jersey area; the Baltimore-Wilmington area; West Virginia; the Cleveland-Detroit area; the Chicago area; St. Louis-Kansas City area; New Orleans-Alabama area; the Houston area; Los Angeles area; and the San Francisco Bay area, as shown in Figure 16. The major production sites by company are listed in Table VII. The distribution of major pesticide* production volume is shown in Figure 17.

The transportation routes for the major pesticides show wide variation. For DDT, for example, the only production site is in the Los Angeles area, but the only major domestic use, at present, is in the cotton states of the South (see Figure 6, p. 23). On the other hand, toxaphene which is used extensively also on Southern cotton is produced in Georgia and trifluralin which is used extensively on Midwestern soybeans (see Figure 7, p. 24), is produced in Indiana. In general, products which have the longer distribution routes probably are transported more often as active ingredients or concentrates and formulated to more dilute levels nearer to the use areas, but practices vary widely and many newer plants include formulation facilities.

---

* Major pesticides refer here to the 22 pesticides selected as representatives in Chapter IV.

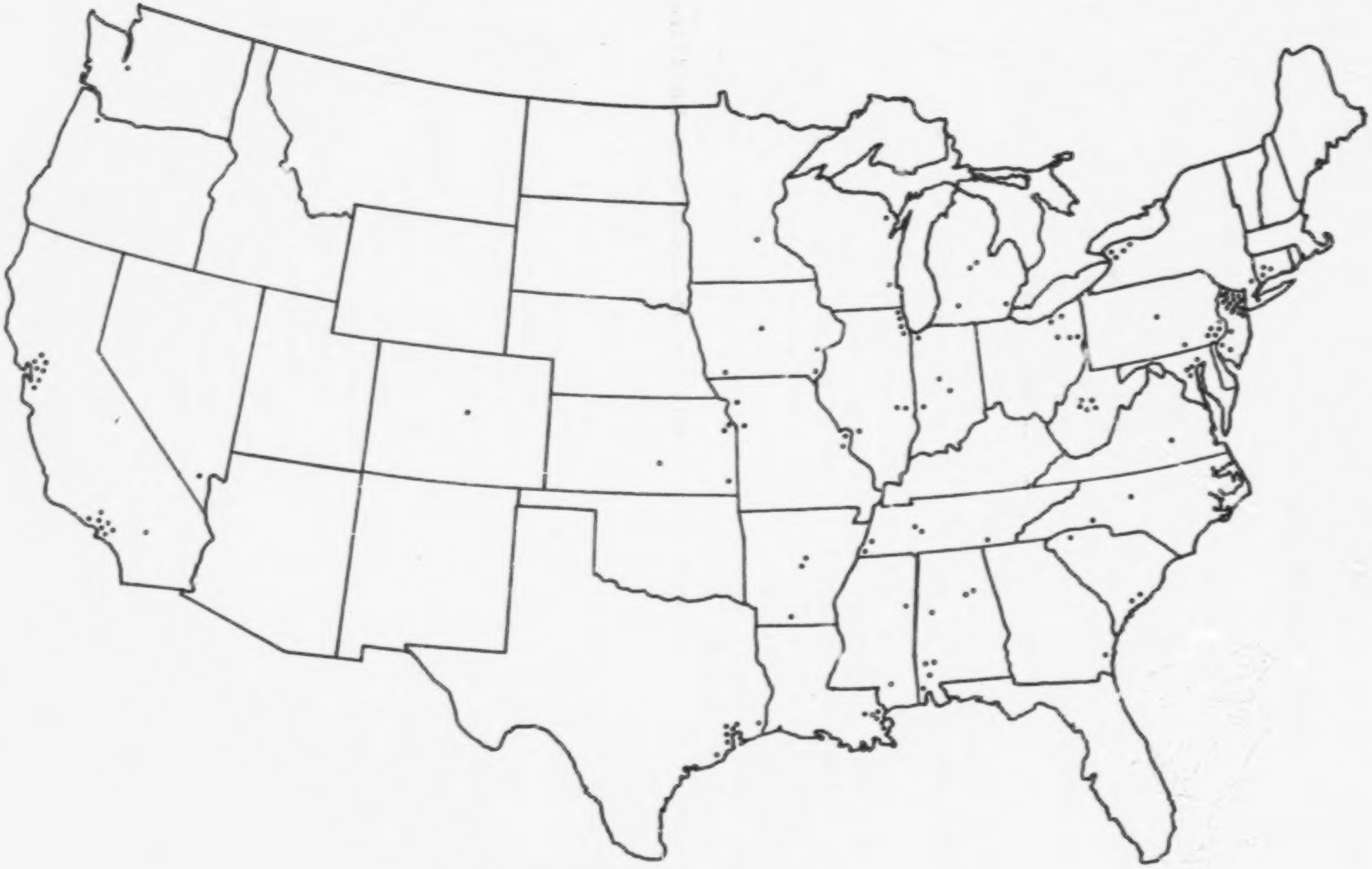


Figure 16 - Locations of Pesticide Production Plants

TABLE VII

MAJOR PESTICIDE PRODUCTION SITES

Company	Production Site
Abbott Laboratories	North Chicago, Illinois
Aceto Chemical Company	Flushing, New York
Alco Chemical Corporation	Whiteford, Maryland; Hanover, Pennsylvania
Allied Chemical Corporation	Baltimore, Maryland; Marcus Hook, Pennsylvania; Carteret, New Jersey
American Cyanamid Company	Warners, New Jersey
Amchem Products, Inc.	Ambler, Pennsylvania; Freemont, California; St. Joseph, Missouri
American Potash & Chemical Company (Subsidiary, Kerr-McGee Corporation)	Los Angeles, California; Hamilton, Mississippi
Ansul Chemical Company	Marionette, Wisconsin
Arapahoe Chemicals Division, Syntex	
Berkeley Chemical Department, Millmaster Chemical Company	Berkeley Heights, New Jersey
Buckman Labs, Inc.	Memphis, Tennessee
Chemagro Corporation	Kansas City, Missouri
Chemical Formulators, Inc.	Nitro, West Virginia
Chemical Insecticide Corporation	Metuchen, New Jersey
Chevron Chemical Company, Ortho Division	Perry Ohio; Fort Madison, Iowa; Richmond, California
Chipman Division, Rhodia, Inc.	Portland, Oregon
W. A. Cleary Corporation	New Brunswick, New Jersey
Commercial Solvents Corporation	Terre Haute, Indiana; Agnew, California
Diamond Shamrock Corporation	Newark, New Jersey; Des Moines, Iowa; Greens Bayou, Texas; Curtis Bay (Baltimore), Maryland
Dow Chemical Corporation	Midland, Michigan; Freeport, Texas; Pittsburg, California
E. I. du Pont de Nemours & Company	East Chicago, Indiana; Deepwater, New Jersey; Linden, New Jersey; La Porte, Texas; Belle, South Carolina

TABLE VII (Continued)

Eli Lilly & Company Elanco Products Division	Indianapolis, Indiana; Lafayette, Indiana
Fairmont Chemical Company	
F.M.C. Niagara Chemical Division	Middleport, New York; Baltimore, Maryland
GAF Corporation, Chemical Division	Linden, New Jersey; Texas City, Texas
Geigy Agricultural Chemicals Division of CIBA-Geigy	St. Gabriel, Louisiana; McIntosh, Alabama; Summit, New Jersey
Glenn Chemical Company, Inc.	Chicago, Illinois
Gordon Corporation	Kansas City, Missouri
Great Lakes Chemical Corporation	El Dorado, Arkansas
Gulf Chemical Division of Gulf Oil Corporation	Pittsburg (Jayhawk), Florida
Guth Chemical Corporation	Hillside, Illinois
Hercules, Inc.	Brunswick, Georgia
Imperial, Inc.	Shenandoah, Iowa
International Minerals & Chemical Corporation	
Mallinckrodt Chemical Works	St. Louis, Missouri; Jersey City, New Jersey
McLaughlin Gormely & King Company	Minneapolis, Minnesota
Merck & Company, Inc.	Rahway, New Jersey; Hawthorne, New Jersey
Michigan Chemicals Corporation	St. Louis, Michigan
Mobil Chemical Company Division Mobil Oil	Richmond, Virginia; Mount Pleasant, Tennessee; Charleston, South Carolina
Monsanto Company	St. Louis, Missouri; Anniston, Alabama; Lauget (E. St. Louis), Illinois; Nitro, West Virginia; Muscatine, Iowa; Luling, Louisiana
Montrose Chemical Corporation	Torrance, California
Morton Chemical Company	
Motomco, Inc.	Clark, New Jersey

TABLE VII (Continued)

Nease Chemical	State College, Pennsylvania; Salem, Ohio
Niklor Chemical Company, Inc.	Long Beach, California
Nutrilite Products, Inc.	Lake View, California
Nor-Am Agricultural Products, Inc.	Chicago, Illinois
Occidental Chemical Company	
Olin Corporation, Agricultural Division	McIntosh, Alabama; Rochester, New York; Little Rock, Arkansas
Ott Chemical Company	
Penick Division, CPC International, Inc.	Montville, New Jersey; Lyndhurst, New Jersey;
Pennwalt Chemicals Corporation	Wyandotte, Michigan
Pfizer, Inc.	Greensboro, North Carolina
Phelps Dodge Refining	
PPG Industries	Barberton, Ohio
Prentiss Drug & Chemical	Newark, New Jersey
Reichold Chemicals, Inc.	Tuscaloosa, Alabama; Tacoma, Washington
Riverdale Chemical Company	Chicago, Illinois
Roberts Chemicals	Nitro, West Virginia
Rohm & Haas Company	Ambler, Pennsylvania; Bristol, Pennsylvania
Shell Chemical Company	Martinex, California; Norco, Louisiana; Denver, Colorado; Mobile, Alabama; Deer Park, Texas; San Ramon, California
Shepard Chemical Company	
Sabin Chemical, Inc.	Niagara Falls, New York
Sanford Chemical Company	Port Neches, Texas
Stauffer Chemical Company	Perry, Ohio; Richmond, California Mount Pleasant, Tennessee; Bucks, Alabama; Henderson, Nevada; Ardsley, New York
Tenneco Chemicals, Inc.	Elizabeth, New Jersey; Long Beach, California

TABLE VII (Concluded)

Thompson-Hayward Chemical Company	Kansas City, Kansas; New Orleans, Louisiana; Brea, Ohio
Troy Chemical Company	Newark, New Jersey
Tull Chemical Company	Oxford, Alabama
Union Carbide Corporation	Institute, West Virginia; South Charleston, West Virginia
Uniroyal Chemical Division, Uniroyal	Gastonia, North Carolina; Geismar, Louisiana; Naugatuck, Connecticut
Universal Oil Products Company	
Upjohn Company	Kalamazoo, Michigan; North Haven, Connecticut
Vanderbilt Chemical Corporation	Bethel, Connecticut
Velsicol Chemical Corporation	Marshall, Illinios; Bayport, Texas; Memphis, Tennessee; Chattanooga, Tennessee
Vineland Chemical Company	Vineland, New Jersey
Vulcan Materials Company Chemical Division	Wichita, Kansas
Wilco Chemical Company, Inc.	
Wood Ridge Chemical Corporation	
Wyandotte Chemical, Division BASF	

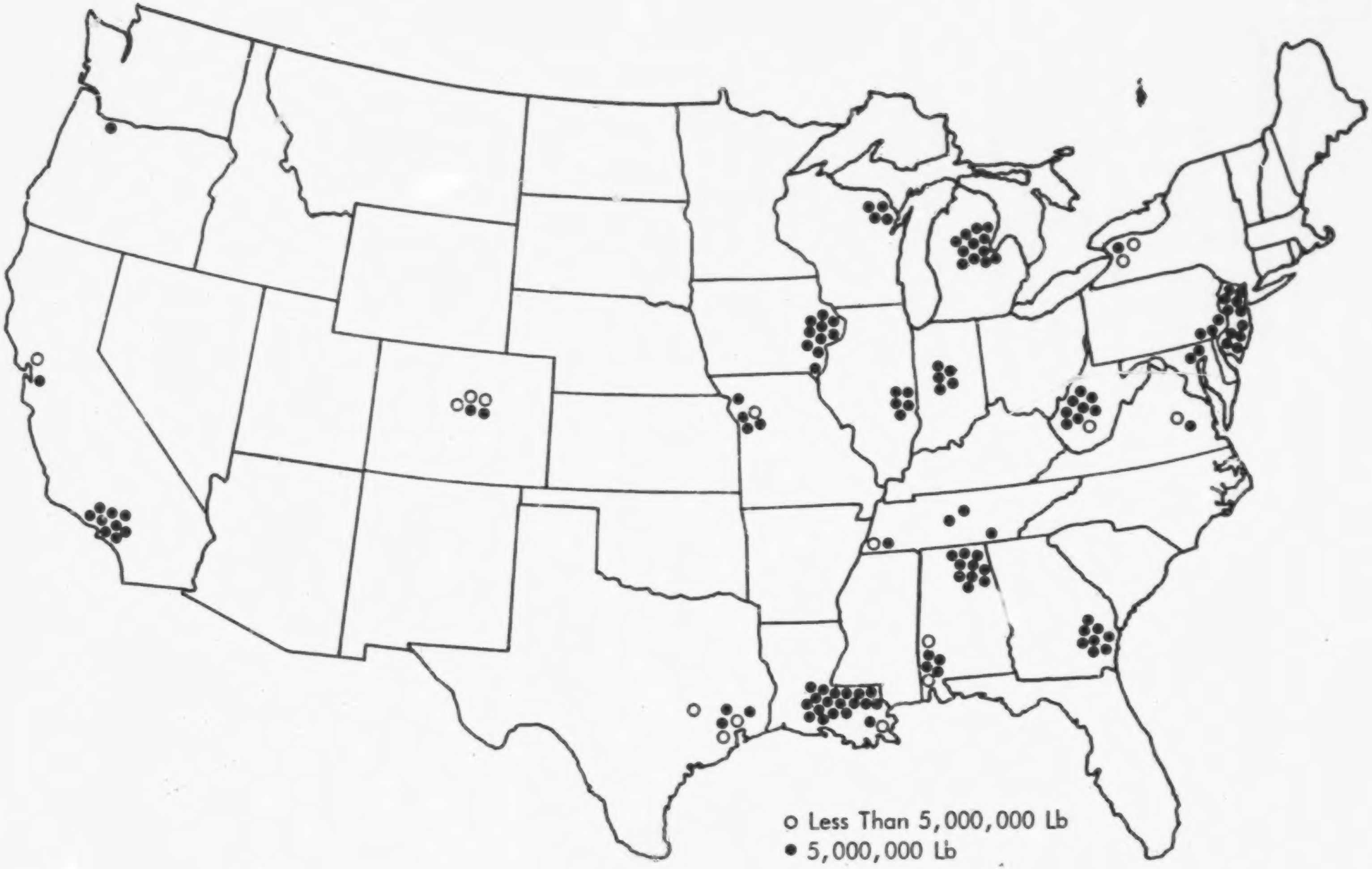

○ Less Than 5,000,000 Lb
● 5,000,000 Lb

Figure 17 - Production Distribution for 22 Major Pesticides

LITERATURE REFERENCES

1. United States Production and Sales of Pesticides and Related Products, 1970, Preliminary, United States Tariff Commission, Washington, D.C., September 1971.

2. Fowler, Lee D., and Harold H. Shepard, The Pesticide Review 1970, U.S. Department of Agriculture, Agricultural Stabilization and Conservation Service, Washington, D.C., 1971.

3. Copeland, Jack G., Statement, "Federal Environmental Pesticide Control Act," U.S. Congress 92nd, 1st Session, Senate Committee on Agriculture and Forestry, Hearings before the Subcommittee on Agricultural Research and General Legislation, U.S. Government Printing Office, Washington, 1971.

4. "Pesticide Use Reports" (Published Quarterly), Department of Agriculture, Sacramento, California.

5. Illinois Agricultural Statistics/Pesticide Use by Illinois Farmers, 1970, Illinois Cooperative Crop Reporting Service, Illinois Department of Agriculture and U.S. Department of Agriculture, Bulletin 71-3, 1971.

6. General Farm Use of Pesticides,1970, Minnesota and Four Other Great Lakes States, Minnesota Department of Agriculture and State-Federal Crop and Livestock Reporting Service, 1971.

7. "Chlorinated Hydrocarbons in the Marine Environment," Report by the Panel on Monitoring Persistent Pesticides in the Marine Environment, Committee on Oceanography, National Academy of Sciences, Washington, D.C., 1971.

IV. MODERN MANUFACTURING METHODS

The number of pesticides produced in the United States is so large that a complete study of the pollution aspects of the production of all of them could not be undertaken under the time requirements of the present program. Therefore, the approach adopted was to select approximately 20 or so key pesticides which would be truly representative of the industry and to make an intensive study of the pollution aspects of their production, transportation, formulation, and marketing. This intensive study approach included plans to visit with knowledgeable company representatives for each of the key pesticides and to visit the actual production plants wherever permitted.

A. Criteria for Selection of Pesticides for Case Studies

Extensive efforts were made to select the key pesticides so that they would be representative of the environmental pollution potential of all pesticides in use. Our consultants Dr. L. E. Cronin and Dr. Gordon Guyer were instrumental in this selection process. Important criteria of production, use, and environmental properties included:

1. Production volume (current and projected).

2. Chemical class of pesticide (chlorinated hydrocarbon, organophosphate, botanical, microbiological, inorganic, etc.).

3. Pesticide class (herbicide, insecticide, fungicide, etc.).

4. Use class (corn, cotton, soybeans, vegetables, public health, right-of-way, etc.).

5. Method of application (fumigant, etc.).

6. Chemical and physical properties (including persistence and accumulation tendencies in the environment).

7. Biological properties (including specificity and biomagnification).

8. Nontarget toxicity (to invertebrates, birds, fish, and mammals).

9. Concern (public or legislative and special health aspects, e.g., mutagenic, teratogenic).

Data for categories 1-9 have already been indicated in Tables II, III, and VI. Toxicity data (mammalian LD_{50}'s) are given in Appendix A for a number of pesticides. Further considerations and ratings for about 60 major pesticides or classes of pesticides were made with the results* indicated in Table VIII.

B. Summary of Classes, Producers, Production, Formulations, and Use Patterns for Case Study Pesticides

On the basis of the considerations in Section IV-A, 22 key pesticides were selected for intensive study. A brief summary of the pesticidal use class and chemical class of these 22 pesticides is given in Table IX. A summary of the producers and production sites is given on p. 72. Tables X, XI, and XII summarize for these 22 products estimated 1971 production volume; formulation site (at manufacturing site or away from it); formulations; major uses; and major areas of use, broken down by five geographical regions of the U. S., U. S. total, and export. These 22 "intensive study" products account for a combined production volume of about 540 million pounds or about 58% of the total U. S. pesticide production.

We estimate that a combined total of about 110 million pounds of these products is exported. DDT has by far the highest export percentage, i.e., about 70% of the total U. S. production. Approximately one-half of the total U. S. production of carbaryl is also exported. Other products of which major quantities are exported include toxaphene, methyl parathion, and malathion. The export of 2,4-D and 2,4,5-T products for military purposes has declined greatly.

Formulation practices by different manufacturers vary, depending on marketing policies. Some companies sell primarily technical active ingredient to formulators who formulate it, alone or with other active ingredients, into products which are marketed under the formulator's label and brand name. In other instances, the basic manufacturer formulates his product(s) himself and distributes and sells it under his own label and brand name. There are many other patterns of formulating, labeling, and product identification and control between these two extremes.

---

* Ratings in Table VIII are on a relative scale with each dot representing a higher level of the property shown. A blank space does not necessarily represent the lowest level, however, but may reflect a lack of data available to the project team and consultants at the time of making the ratings.

TABLE VIII

PESTICIDE RATINGS

	I Volume		II Chemical and Physical Properties		III Biological Properties		IV Toxicity					V Concern	
	Present	Potential	Persistent	Phesophile	Wide Spectrum	Magnified	Invert.	Birds	Fish	Mammal	Human	Recommend	Popular
Actidione										••			
Aldrin	••••	••	••••	••	•••	•••		••	•••	•••	•••	•••	••
Amiben		•••											
Acrolein (Aqualin)										•••			
Arsenic Compounds										•••		•••	
BHC			••					••	•••	••		•••	
Bidrin										•••			
Calcium Arsenate										•••			
Captan	•	•••	••	••						••			
Carbamate	•	••											
Chlordane	•	•	•••	••	•••			••	•••	••		•••	
Copper Sulfate	•••									••			
Cyanide										••••			
Diazinon	•	•••			••								
DDD				••		•••		••	••			•••	••
DDT	••••	-	••••	••	•••	•••	•••	•••	•••	•••		•••	••••
DDVP										•••			
Delnav										•••			
Dieldrin	•••		••••	•••	•••	•••		••••	••••	••	•••	•••	•••
Disulfoton (Di-Syston)				••						•••			
Endrin	•	••	••••	•••	•••	•••	••	•••	•••	•••		•••	•••
EPN				••					••	•••			
Guthion (Azinphosmethyl)	•	•••			•••								

TABLE VIII (Continued)

	I Volume		II Chemical and Physical Properties		III Biological Properties		IV Toxicity					V Concern	
	Present	Potential	Persistent	Phasophile	Wide Spectrum	Magnified	Invert.	Birds	Fish	Mammal	Human	Recommend	Popular
Heptachlor	•	-	••••		•••	••	••	•••	•••	•••		•••	
Lead Arsenate										••••		•••	
Lindane	••			••						•••		•••	
Malathion	•	•••											
Methyl Bromide	•												
Mercury Fungicides	••									••		•••	•••
Methyl Parathion	•••	••								•••			
Mirex										••			
Parathion	•	-	••	••			•••		••••	•••	••••		
Pentachlorophenol (PCP)	•••			••	••					••			
Mevinphos (Phosdrin)										••••			
Nitralin (Planavin)	•	••••											
Pyrethrum									••	••			
Ramrod	•	•••											
Carbaryl (Sevin)	•	•••											
Sodium Arsenate							••		••••		••••		
Sodium Chlorate	•••									••	•		
Sodium Fluoroacetate (1080)										••••			
Strobane										••			
Strychnine										•••			
Demeton (Systox)										••••			
TEPP										••••			
Phorate (Thimet)			••							••••			
Toxaphene	••••	••	••	••	••	•••		•••	••••	•••		•••	

TABLE VIII (Concluded)

	I Volume		II Chemical and Physical Properties		III Biological Properties		IV Toxicity					V Concern	
	Present	Potential	Persistent	Phasophile	Wide Spectrum	Magnified	Invert.	Birds	Fish	Mammal	Human	Recommend	Popular
Zinc Phosphide										●●●			
Zinophos										●●●			
Amitrole										●●●	●●		
Atrazine	●	●●											
2,4-D	●●●●	●●●											
Dinitro Compounds							●●			●●●			
2,4,5-T	●●●●	●●●								●●	●●		
Picloram (Tordon)	●	●●●●											
Trifluralin (Treflan)	●	●●●●											

TABLE IX

USES AND CLASSES OF SELECTED PESTICIDES

	Pesticidal Use Class				Chemical Class							
Selected Pesticides	Fungicides	Fumigants	Herbicides	Insecticides	Chlorinated Hydrocarbons	Triazines	Carbamates	Aryl Organo-Phosphates	Aliphatic Organo-Phosphates	Inorganics	Biologicals	Other
Alachlor (Lasso)			H									X
Aldicarb (Temik)				I			X					
Aldrin-Dieldrin				I	X							
Atrazine			H			X						
B. thuringiensis				I							X	
Captan	F											X
Carbaryl (Sevin)				I			X					
Chlordane				I	X							
2,4-D			H		X							
DDT				I	X							
Disulfoton				I					X			
Malathion				I					X			
Mercury Fungicides	F									X		
Methyl Bromide		Fu										X
Methyl Parathion				I				X				
Parathion				I				X				
Phorate (Thimet)				I					X			
Pyrethrins				I								X
2,4,5-T			H		X							
Toxaphene				I	X							
Trifluralin (Treflan)			H									X

TABLE X

SELECTED HERBICIDES, ESTIMATED PRODUCTION VOLUME, FORMULATION, USES, AND AREAS OF USE, 197

Product	Annual Prod. (MM lb)	Plant Site Form.a/	Formulations (%)b/				Major Uses	Areas of Use (MM lb, a.i.)c/						
			EC	G	WP	Other		E	SE	MW	S	W	U.S.	Export
Atrazine	90	100	< 5	-	95	-	Corn>>Sorgham> Indust.	4	8	60	9	4	85	5
2,4-D	45	20	100	-	-	-	Small grains, Corn,H&G	3	3	22	3	8	39	6
Trifluralin	25	90	>> 95	-	-	<< 5	Soybeans>Cotton	1	5	9	6	1	22	3
Alachlor	20	95	70	30	-	-	Corn, Soybeans	-	2	14	2	-	18	2
2,4,5-T	6	0	100	-	-	-	Pasture, Brush Control	-	1	1	2	1	5	1

---

a/ Percent of active ingredient formulated at manufacturing site.

b/ Percent of active ingredient (a.i.) formulated as emulsifiable concentrate (EC), granular (G), wettable powder, including dust concentrate (WP), or into other formulations.

c/ Definition of symbols:

E - Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut, New York, New Jersey, Pennsylvania

SE - Delaware, Maryland, Virginia, West Virginia, North Carolina, South Carolina, Georgia, Florida

MW - Ohio, Indiana, Illinois, Michigan, Wisconsin, Minnesota, Iowa, Missouri, North Dakota, South Dakota, Nebraska, Kansas

S - Kentucky, Tennessee, Alabama, Mississippi, Arkansas, Louisiana, Oklahoma, Texas

W - Montana, Idaho, Wyoming, Colorado, New Mexico, Arizona, Utah, Nevada, Washington, Oregon, California, Hawaii, Alaska

TABLE XI

SELECTED CHEMICAL INSECTICIDES, ESTIMATED PRODUCTION VOLUME, FORMULATIONS, USES, AND AREAS OF USE, 1971

Product	Annual Prod. (MM lb)	Plant Site Form.[a/]	Formulations (%)[b/] EC	G	WP	Other	Major Uses	Areas of Use (MM lb, a.i.)[c/] E	SE	MW	S	W	U.S.	Export
Toxaphene	50	0	95	-	5	-	Cotton, other crops, livestock	-	8	5	25	4	42	8
DDT	45	50	< 5	-	95	-	Cotton	-	2	<1	9	<1	12	33
Carbaryl	45	0	-	-	> 95	< 5	Cotton, many other crops	3	3	5	8	4	23	22
Me-parathion	45	< 5	100	-	-	-	Cotton, many other crops	1	8	2	20	2	33	12
Malathion	35	Negl.	100	-	-	-	Many crops, H&G	6	4	8	3	4	25	10
Chlordane	25	5	100	-	-	-	Many crops, PCO, H&G	All Areas					23	2
Parathion	15	< 5	100	-	-	-	Fruit, many other crops	1	2	3	2	3	11	4
Aldrin	10	0	10	80	-	10	Corn	-	-	10	-	-	10	Negl.
Disulfoton	8	60	30	60	-	10	Corn, cotton, small grains	0.5	1	4	2	0.5	8	Negl.
Phorate	8	0	10	90	-	-	Corn, cotton	1	1	4	1	1	8	Negl.
Aldicarb	3	0	-	100	-	-	Cotton, sugar beets	-	0.2	0.2	2	0.6	3	Negl.
Dieldrin	< 1	0	80	-	-	20	PCO, industrial	All Areas					0.5	Negl.

---

a/ Percent of active ingredient formulated of manufacturing site.

b/ Percent of active ingredient (a.i.) formulated as emulsifiable concentrate (EC), granular (G), wettable powder, including dust concentrate (WP), or into other formulations.

c/ See Table X, p. 68 for definition of symbols.

TABLE XII

SELECTED BIOLOGICAL INSECTICIDES, FUMIGANTS, AND FUNGICIDES: ESTIMATED PRODUCTION VOLUME, FORMULATIONS, USES AND AREAS OF USE, 1971

Product	Annual Prod. (MM lb)	Plant Site Form.[a]	Formulations (%)[b]				Major Uses	Areas of Use (MM lb, a.i.)[c]						
			EC	G	WP	Other		E	SE	MW	S	W	U.S.	Export
Biology and Botanical Insecticides														
B. thuringiensis	1.5	100	-	-	100	-	Vegetable crops	0.1	0.1	0.1	0.2	0.5	1	0
Pyrethrins	0.3	50	< 10	-	-	> 90	Household insects	All Areas					0.3	0
Fumigant														
Methyl bromide	22	0[d]	-	-	-	100	Tobacco, other seedbeds, stored grain	1	8	9	2	3	23	2
Fungicides														
Captan	18	0	-	-	100	-	Decid. fruit, many other crops, H&G	5	3	5	2	3	18	Negl
Hg-fungicides	0.06[e]	0[e]	-	~ 50	~ 50		Turf	All Areas					0.06[c]	Negl

---

[a] Percent of active ingredient formulated at manufacturing site.

[b] Percent of active ingredient (a.i.) formulated as emulsifiable concentrate (EC), granules (G), wettable powder, including dust concentrate (UP), or into other formulations.

[c] See Table X, p. 68 for definition of symbols.

[d] Not formulated, but warning agent is added to some of packaged material.

[e] Production given as Hg content; formulated at producer's plant at another location.

Types of formulations also vary considerably, within the limits set by the physical and chemical properties of the different active ingredients. Granular formulations are popular for corn insecticides and at least one corn herbicide, alachlor. For products to be sprayed, emulsifiable concentrates are usually preferred over wettable powders because of greater ease of measuring and handling and less trouble with nozzle clogging. However, atrazine, by far the biggest of all herbicides was until recently available only as a wettable powder. This has obviously not prevented it from gaining its dominant position as a corn herbicide. Apparently, pesticide users will accept certain handling inconveniences in return for superior performance.

Most cotton insecticides are applied as sprays and consequently, emulsifiable concentrate formulations predominate among cotton insecticides.

Considering all of the "intensive study" pesticides combined, the midwestern states, according to our estimates, account for approximately 40% of the domestic consumption of these products. Of the balance, about 26% were used in the southern states, 15% in the southeastern states, 11% in the western states and 8% in the eastern states. This distribution pattern reflects the extensive use of pesticides on midwestern farm crops, especially corn and soybeans, and on cotton in the southern and southeastern states.

It must be emphasized that these figures represent the distribution pattern of only 22 selected pesticides. Similar information for all pesticides might indicate a somewhat different geographical distribution, although we believe that it would not be too drastically different. In the past, the western states, especially California, accounted for a relatively larger share of total pesticide consumption. However, the greatest increase in pesticide use has been in herbicides, and herbicide use in turn has increased most in the midwestern states. This explains the increase in the midwest's share of total pesticide consumption.

C. Case Studies

Following the selection of the 22 key pesticides for intensive study the major producers of these materials were contacted* and requests made for an interview with individuals who would be knowledgeable about the manufacturing processes and waste disposal practices for these pesticides. A tour of the production facilities was also requested. The producers and types of visits conducted are summarized in Table XIII.

---

* The cooperation of the National Agricultural Chemicals Association is appreciated.

TABLE XIII

CASE STUDIES: SUMMARY OF PRODUCERS VISITED

Pesticide	Producer Visited	Production Facilities
Alachlor	Monsanto Company	Muscatine, Iowa[a]
Aldicarb	Union Carbide Corporation	Institute, West Virginia[a]
Aldrin-dieldrin	Shell Chemical Company	Denver, Colorado
B. thuringiensis	Abbott Laboratories Nutrilite Products	North Chicago, Illinois[b] Buena Park, California[a]
Atrazine	Geigy Agricultural Chemicals	St. Gabriel, Louisiana[a]
Captan	Calhio Chemical Company	Perry, Ohio
Carbaryl	Union Carbide Corporation	Institute, West Virgina[a]
Chlordane	Velsicol Chemical Corporation	Marshall, Illinois
2,4-D	Dow Chemical Company Chipman Division, Rhodia, Inc.	Midland, Michigan Portland, Oregon[a]
DDT	Montrose Chemical Corporation	Torrance, California[b]
Disulfoton	Chemagro Corporation	Kansas City, Missouri[b]
Malathion	American Cyanamid Company	Warner, New Jersey
Mercury fungicides	Mallinckrodt Chemical Works	St. Louis, Missouri and Jersey City, New Jersey
Methyl bromide	Dow Chemical Company	Midland, Michigan
Methyl parathion	Monsanto Company	Anniston, Alabama[a]
Parathion	Monsanto Company	Anniston, Alabama[a]
Phorate	American Cyanamid Company	Warner, New Jersey[a]
Pyrethrins[c]	FMC, Niagara Chemical Division	Baltimore, Maryland[b] and Middleport, New York[a]
2,4,5-T	Dow Chemical Company Thompson-Hayward Chemical Company	Midland, Michigan Kansas City, Kansas
Toxaphene	Hercules, Inc.	Brunswick, Georgia[a]
Trifluralin	Elanco Products Company	Indianapolis, Indiana[a]

---

a/ Interview at home office or elsewhere.

b/ Plant tour provided.

c/ Information also furnished by McLaughlin Gormley King Company, Minneapolis, Minnesota.

The results of the key pesticide studies are tabulated in Case Studies 1 through 22 arranged as shown in Table XIV. Each study summarizes the process chemistry, a schematic depiction of the production and waste disposal system, the movement of raw materials to the production site, the disposal of by-products and waste products, the movement of technical and formulated products from the production site, and other information pertinent to pollution potential. Special note is made here that the production diagrams shown for many products were not provided by the producer: these were prepared by the authors for descriptive purposes and may not represent all or the exact process steps in use. Similarly, the percentage yield of active ingredient or a complete materials balance were not revealed by the producers because of proprietary considerations and the data shown are author estimates. Unfortunately the effluent data being submitted by producers under the 1899 Refuse Disposal Act have not become available in significant amounts in time for inclusion in the study.

TABLE XIV

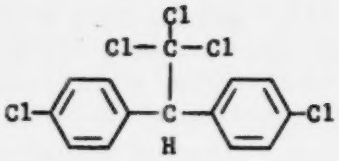
ORDER OF PRESENTATION OF CASE STUDIES

Case Study	Pesticide	Class
1	DDT	Insecticide, chlorinated hydrocarbon
2	Aldrin	Insecticide, chlorinated hydrocarbon
3	Dieldrin	Insecticide, chlorinated hydrocarbon
4	Chlordane	Insecticide, chlorinated hydrocarbon
5	Toxaphene	Insecticide, chlorinated hydrocarbon
6	Disulfoton	Insecticide, alkyl organophosphorous
7	Malathion	Insecticide, alkyl organophosphorous
8	Phorate	Insecticide, alkyl organophosphorous
9	Parathion	Insecticide, aryl organophosphorous
10	Methyl parathion	Insecticide, aryl organophosphorous
11	Carbaryl	Insecticide, carbamate type
12	Aldicarb	Insecticide, carbamate type
13	2,4-D	Herbicide, chlorinated phenoxy
14	2,4,5-T	Herbicide, chlorinated phenoxy
15	Atrazine	Herbicide, triazine
16	Trifluralin	Herbicide, nitroaryl
17	Alachlor	Herbicide, amide type
18	Captan	Fungicide, chloroalkylthio type
19	Methyl bromide	Fumigant, halogenated
20	Pyrethrin	Insecticide, botanical
21	*Bacillus thuringiensis*	Insecticide, microbiological
22	Mercury chlorides	Fungicide, inorganic

CASE STUDY NO. 1

Pesticide: DDT

Chemical name and formula:



1,1,1-Trichloro-2,2-bis(p-chlorophenyl) ethane

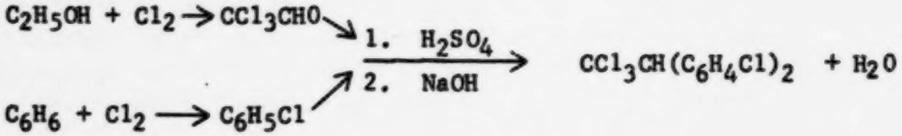
Chemical class: Chlorinated hydrocarbon

Pesticide class: Broad spectrum insecticide

Description: Solid; nearly insoluble in water; moderately toxic; persistent

Producers: Montrose (Torrance, California)

Production chemistry:



$$C_2H_5OH + Cl_2 \rightarrow CCl_3CHO$$
$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl$$
$$CCl_3CHO + C_6H_5Cl \xrightarrow[\text{2. NaOH}]{\text{1. } H_2SO_4} CCl_3CH(C_6H_4Cl)_2 + H_2O$$

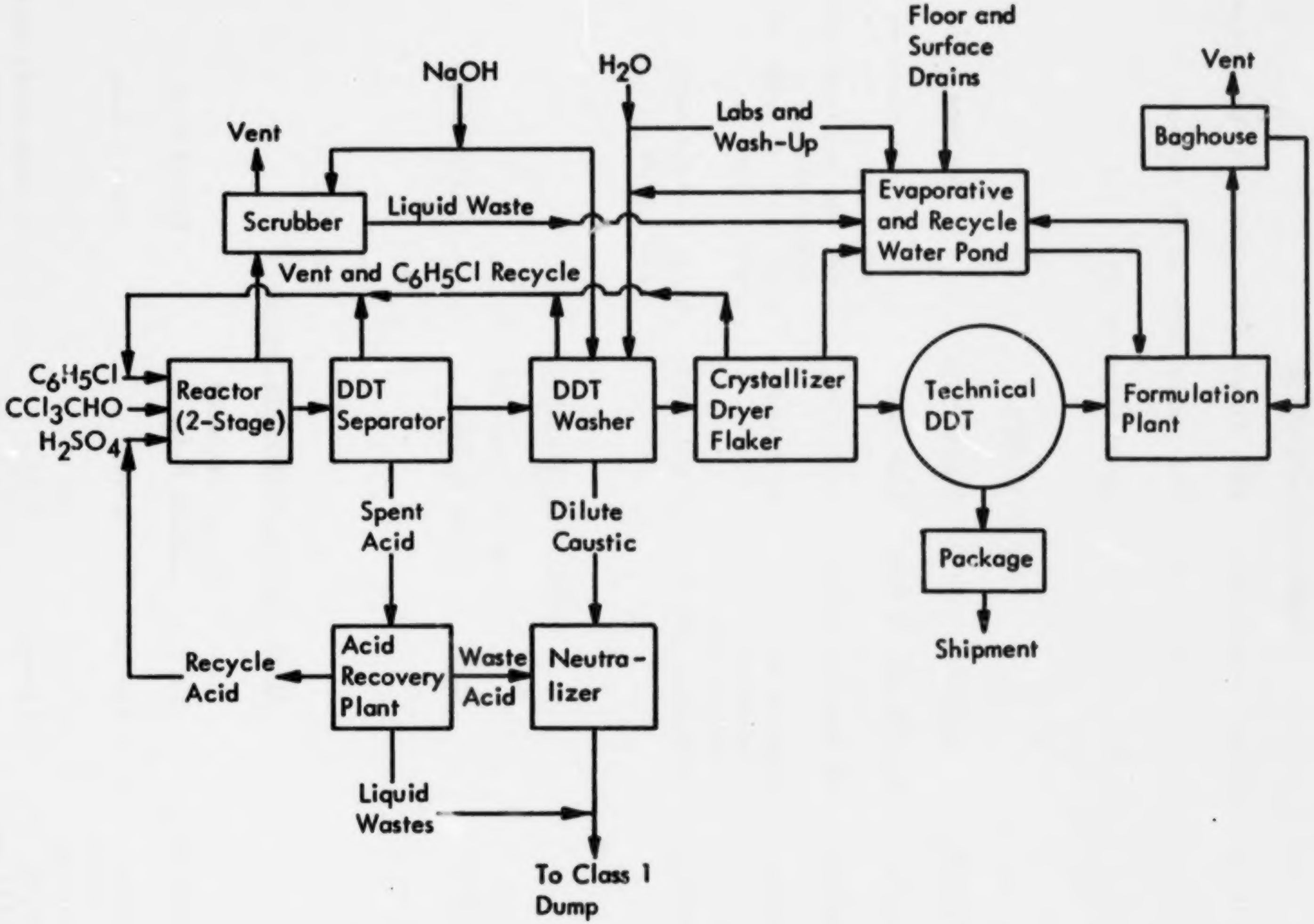

NaOH
H_2O
Floor and Surface Drains
Vent
Labs and Wash-Up
Vent
Baghouse
Scrubber
Liquid Waste
Evaporative and Recycle Water Pond
Vent and C_6H_5Cl Recycle
C_6H_5Cl
CCl_3CHO
H_2SO_4
Reactor (2-Stage)
DDT Separator
DDT Washer
Crystallizer Dryer Flaker
Technical DDT
Formulation Plant
Spent Acid
Dilute Caustic
Package
Shipment
Recycle Acid
Acid Recovery Plant
Waste Acid
Neutra-lizer
Liquid Wastes
To Class 1 Dump

Figure 18 - Production and Waste Schematic for DDT

Production Equipment

Process continuity: semibatch

Est. Annual production: 45 MM lb/year

Equipment dedication: DDT only

Plant capacity: 81 MM lb/year

Equipment age: Not available

Formulation on site: Yes

Raw Materials

Material	Received From	Received By	Storage
1. Choral	Henderson, Nevada	Tank cars	Steel storage tanks on plant site
2. C_6H_5Cl	Henderson, Nevada	Tank cars	Steel storage tanks on plant site
3. Oleum	Compton or Dominques, California	Tank trucks	Steel storage tanks on plant site
4. Caustic	Henderson, Nevada	Tank trucks	Steel storage tanks on plant site

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. None			
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient	Aqueous	Unknown	Class 1 dump
2. Solvents			
3. Na_2SO_4	Aqueous	0.87	Holding pond, recycle
4. Solid waste		10-15 cu yd	Class 1 dump

Disposition of Technical and Formulated Products

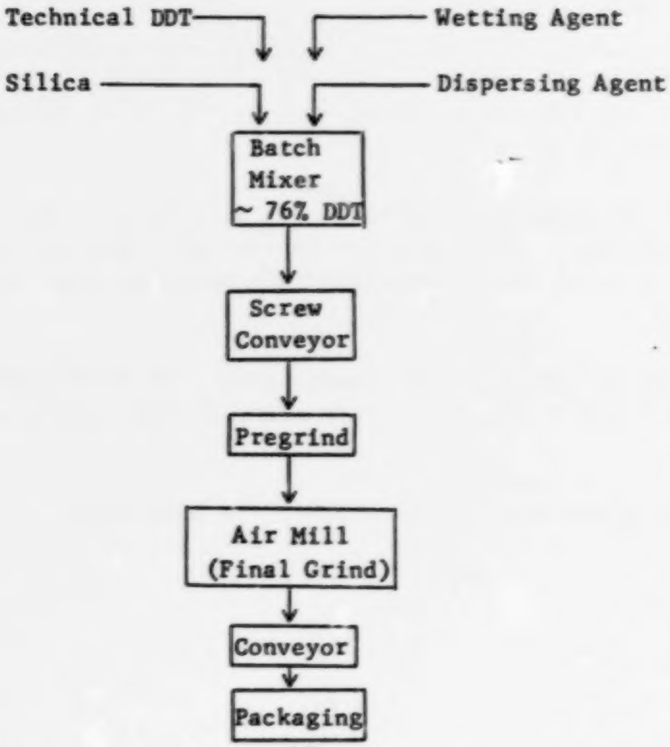
	Shipments				
	Technical Product		Formulated Products		
Warehouse On Site	Container	Transportation	Formulation	Container	Transportation
X	50 lb bags	Boxcar	WP (75% A.I.)	100-200 lb lined fiber drums and 75 lb boxes	Truck for export via Los Angeles; boxcar for other destinations

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ___Yes _X_No

Other regulations apply: The Department of Occupational Health, Air Pollution Control District, the Water Resources Control Board (state and regional), and the Los Angeles Sanitation Districts (city and county) are active in pollution control.

Formulation: A 75% wettable powder DDT is formulated for WHO and AID according to the following process.


Technical DDT
Wetting Agent
Silica
Dispersing Agent
Batch Mixer ~ 76% DDT
Screw Conveyor
Pregrind
Air Mill (Final Grind)
Conveyor
Packaging

Hoods are located at points having emissions potential and exhaust under vacuum to a baghouse. No scrubbers are used. Liquid formulations are no longer being made.

Pollution control: The process portion of the plant has no liquid waste outfall. Much of the water from the process goes to an open, concrete-lined evaporative holding pond and is recycled. All drains and process sewers have been isolated from the city sewer system. Only sanitary waste and boiler blowdown water go to the city sewers. The restroom lavatory basins, however, discharge to the holding pond system. Water consumption has been reduced from 20 million to 1.5 million gallons per month. Water from the recycle pond is also used for cooling water without filtration. This practice has caused no problem to date. The "recycle" water typically contains 10 to 15 ppm DDT.

From 20,000 to 25,000 gallons per day of liquid waste are generated from the neutralization step and are removed by truck to a Class 1 dump. Some 10 to 15 cu yd/day of solid waste bags, empty containers, etc., are also taken to this dump by a commercial disposal service. All vents from the second stage of the reactor are NaOH scrubbed and the liquid goes to the recycle water pond. Equipment washdown is not a problem as this is normally done only during shutdowns. Wash water goes to the recycle pond. Spills and leakers have not been a major problem. One spill occurred when a truck carrying technical material had an accident and spilled DDT. The material was picked up along with the top 3 in. of soil and disposed of.

Prior to the modification of the waste treatment facilities DDT losses from this plant were apparently fairly high: DDT levels of 70 ppb were observed[1/] in the river below the plant and 0.5 million pounds sediments from the river containing about 4,500 lb of DDT have been dredged up for treatment.[2/]

Quality control: Montrose maintains its own quality control lab for routine analyses. Setting point is the major quality control used. To date they have had no off-specification material that could not be reworked.

Personnel safety: No unusual safety or hazard problems are associated with DDT production. Standard personnel safety equipment are used.

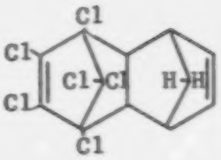
This plant does not come under the 1899 Act.

General information: Montrose is the only DDT producer left in the U. S. and only about 10 million pounds per year are used domestically. Major use areas are the cotton states: Arkansas, Mississippi, Texas, and Louisiana. Montrose does have intrastate registration in California for alfalfa seed, citrus, peppers, onions, and public health purposes. Major domestic DDT formulators are, Helena Chemical and Valley Chemical (Mississippi), Olin (Arkansas), and Micro Chemical (Louisiana).

CASE STUDY NO. 2

Pesticide: Aldrin

Chemical name and formula:


Cl
Cl
Cl1-Cl
H-H
Cl
Cl

1,2,3,4,10,10-Hexachloro-1,4,4a,
5,8,8a-hexahydro-1,4-endo-exo-
5,8-dimethanonaphthalene

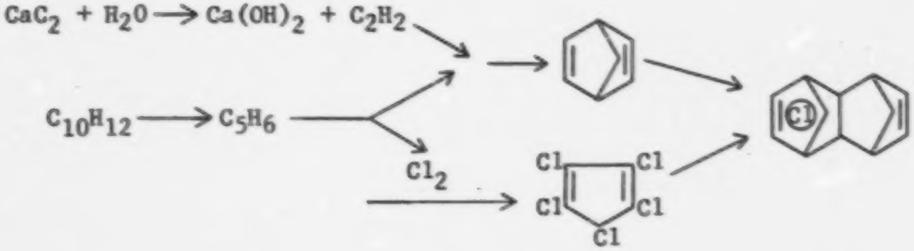
Chemical class: Chlorinated hydrocarbon

Pesticide class: Broad spectrum insecticide

Description: Solid, insoluble in water, very toxic; persistent in form of dieldrin

Producers: Shell (Rocky Mountain Arsenal, Colorado)

Production chemistry:


CaC2 + H2O → Ca(OH)2 + C2H2
C10H12 → C5H6
Cl2
Cl
Cl
Cl
Cl
Cl
Cl

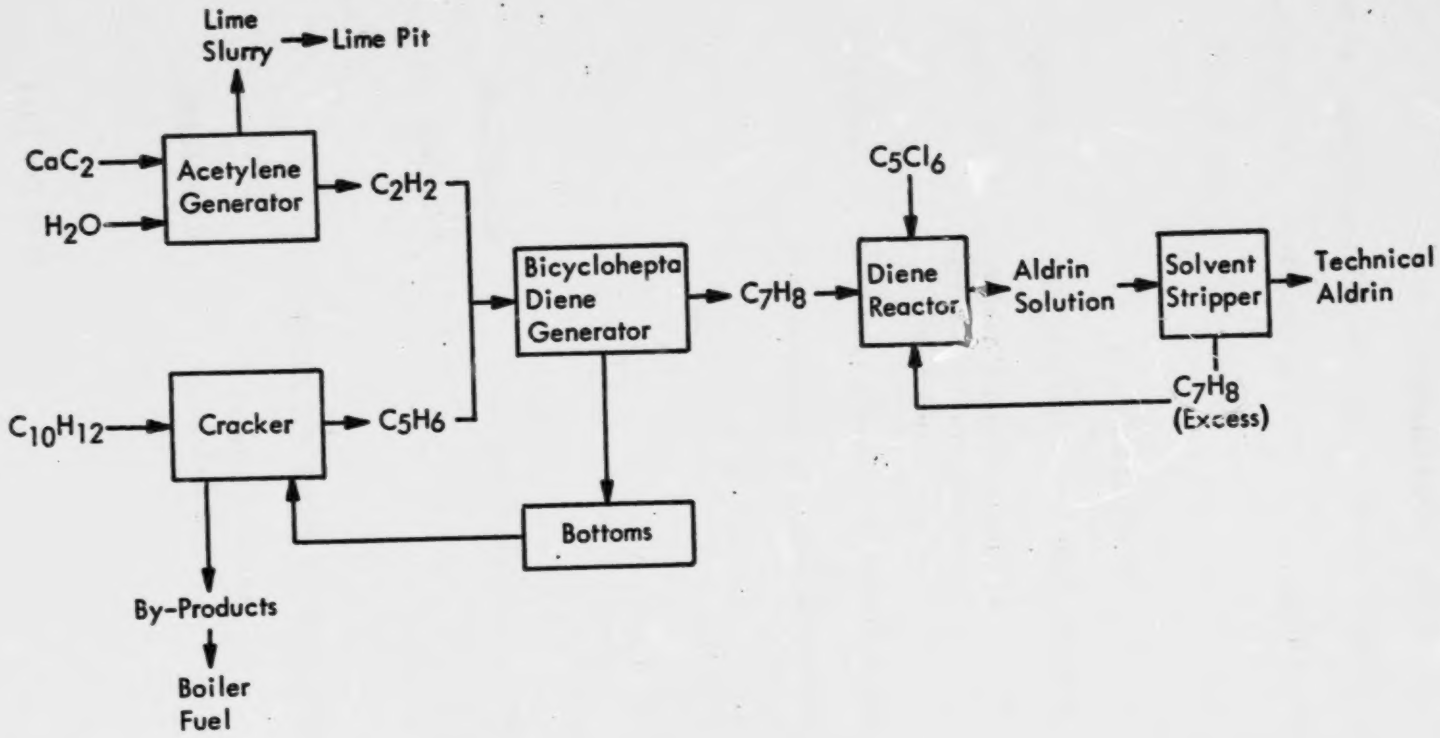

Lime Slurry
Lime Pit
CaC_2
H_2O
Acetylene Generator
C_2H_2
$C_{10}H_{12}$
Cracker
C_5H_6
By-Products
Boiler Fuel
Bicyclohepta Diene Generator
Bottoms
C_7H_8
C_5Cl_6
Diene Reactor
Aldrin Solution
Solvent Stripper
Technical Aldrin
C_7H_8 (Excess)

Figure 19 - Production and Waste Schematic for Aldrin

Production Equipment

Process continuity: Semicontinuous

Est. Annual production: 11 MM lb/year

Equipment dedication: Aldrin

Plant capacity: ~ 25 MM lb/year

Equipment age:

Formulation on site: ~ 10%

Raw Materials

Material	Received From	Received By	Storage
1. Calcium carbide	Oregon; Midwest	Rail & gondola car (12 2-ton containers/car)	Tote bins
2. Dicyclopentadiene	Baton Rouge	Rail, tank cars	Tank cars
3. Hexachlorocyclopentadiene	Niagara Falls	Rail, tank cars	
4. Petroleum solvent (for formulation)	Houston	Rail, tanks	

Reactions By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. $Ca(OH)_2$	Slurry	0.202	Lime pit
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			
3. Hydrocarbons			Used for fuel

Disposition of Technical and Formulated Products

	Shipments				
Warehouse	Technical Product[a]		Formulated Products		
On Site	Container	Transportation	Formulation	Container	Transportation
X	28 Gal. fiber Mylar-lined drums	Truck and rail	10% of product, E.C. form	5, 30 and 55 gal. lined drums	Mostly trucks

---

[a] Approximately 90% of production is shipped as technical and is nearly all formulated to granules.

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ____Yes _X_No

Other regulations apply:

Pollution control: No liquid waste streams contain aldrin. Small amounts of aldrin-containing liquid wastes from spill cleanup or floor washings would go to a 100-acre asphalt-lined evaporation basin on the arsenal. This basin is capable of evaporating 150 gal. of water per minute year-round and has shown no signs of leaks in its 16 years of use. The arsenal is also diked so that all surface waters go to unlined storage basins. During shutdown the aldrin unit would be washed with toluene and the washings would go to dieldrin manufacture. Damaged drums containing aldrin would be similarly cleaned, then incinerated, flattened and sold as scrap steel. Some wipe cloths are burned, some are cleaned. Have had no railroad accidents in shipping aldrin.

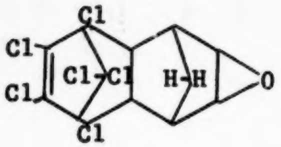
Quality control: No significant impurities or off-specification problems with aldrin and no shelf life problems. The drums for the E.C. receive a statistical leak inspection, which goes to 100% inspection if a lot looks poor. Biggest problem is rub-off of part of drum label.

Personnel: Production workers are trained. Production is seasonal with a shutdown usual in summer, but production workers are utilized elsewhere. Workers get a pre-employment physical, and monthly cholinesterase test because of related work on organophosphate pesticides. Workers receive clean coveralls daily, which are sent along with wipe cloths to a commercial laundry where they are said to be handled separately.

CASE STUDY NO. 3

Pesticide: Dieldrin

Chemical name and formula:



1,2,3,4,10,10-Hexachloro-6,7-
epoxy-1,4,4a,5,6,7,8,8a-
octahydro-1,4-endo-exo-5,8-
dimethanonaphthalene

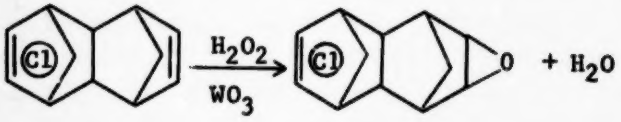
Chemical class: Chlorinated hydrocarbon

Pesticide class: Broad spectrum insecticide

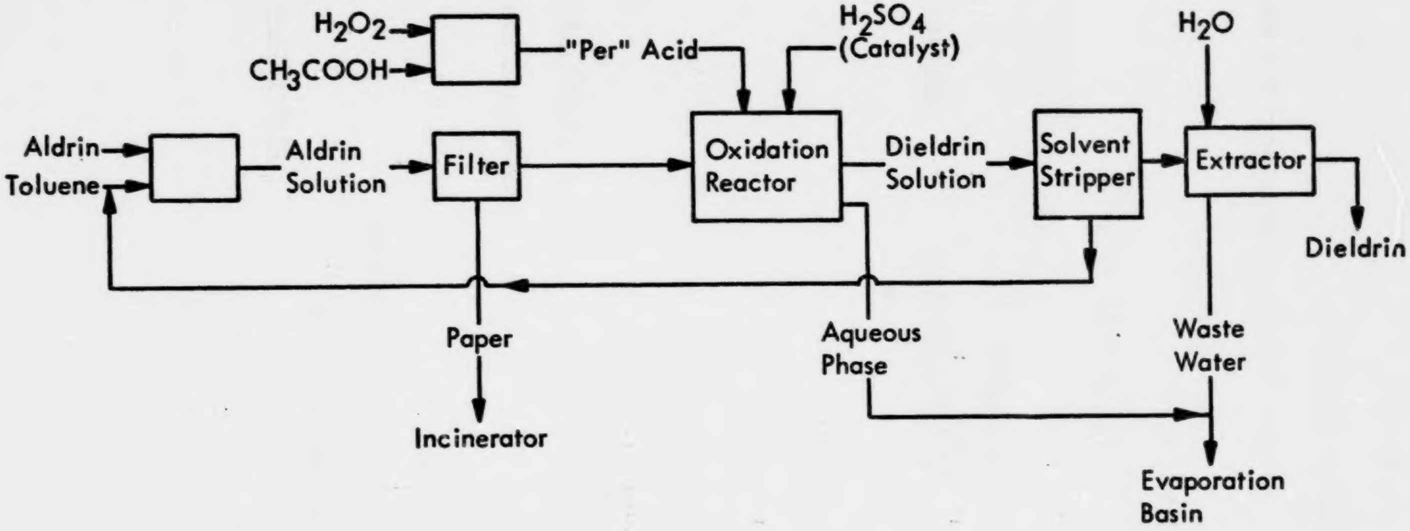
Description: Solid; insoluble in water; very toxic; persistent

Producers: Shell (Denver, Colorado).

Production chemistry:



Aldrin Dieldrin



H_2O_2
CH_3COOH
"Per" Acid
H_2SO_4 (Catalyst)
H_2O
Aldrin
Toluene
Aldrin Solution
Filter
Oxidation Reactor
Dieldrin Solution
Solvent Stripper
Extractor
Dieldrin
Paper
Incinerator
Aqueous Phase
Waste Water
Evaporation Basin

Figure 20 - Production and Waste Schematic for Dieldrin

Production Equipment

Process continuity:	Est. Annual production: 0.5 MM lb
Equipment dedication: O-P products also	Plant capacity:
Equipment age:	Formulation on site:

Raw Materials

Material	Received From	Received By	Storage
1. Aldrin	On site		
2. Toluene			
3. Acetic acid			
4. H_2O_2			

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Water			Evaporation basin
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			
3.			

Disposition of Technical and Formulated Products

	Shipments				
Warehouse	Technical Product[a/]		Formulated Products		
On Site	Container	Transportation	Formulation	Container	Transportation
Some (drums)	30 Gal. drums	Rail and truck (in less than full lots)	None		

---

a/ Mostly used for termite control now.

Pollution Control Regulation

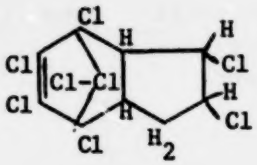
1899 Refuse Disposal Act applies to this manufacture ____Yes _X_ No

Pollution control: Liquid wastes go to evaporation basin (see aldrin, case study 2). A small amount of solid waste, including filter paper, is burned in a smokeless-type incinerator. Equipment cleanup with toluene, which is apparently saved. See aldrin for further remarks.

CASE STUDY NO. 4

Pesticide: Chlordane

Chemical name and formula:



Mixture of octachloro-4,7-methanotetra-hydroindane and related compounds

Chemical class: Chlorinated hydrocarbon

Pesticide class: Broad spectrum insecticide

Description: Solid, insoluble in water; moderately toxic

Producers: Velsicol (Marshall, Illinois)

Production chemistry: The process reactions are approximately as follows:

Naptha $\longrightarrow$ Cyclopentadiene (C_5H_6)
Cl_2 + NaOH (aq.) $\longrightarrow$ NaClO (aq.)
NaClO (aq.) + C_5H_6 $\longrightarrow$ C_5Cl_6 + NaCl (alk. soln)
C_5Cl_6 + C_5H_6 $\longrightarrow$ Chlordene ($C_{10}H_6Cl_6$)
Chlordene + Cl_2 $\longrightarrow$ Tech. chlordane ($C_{10}H_6Cl_8$ + related cpds.)

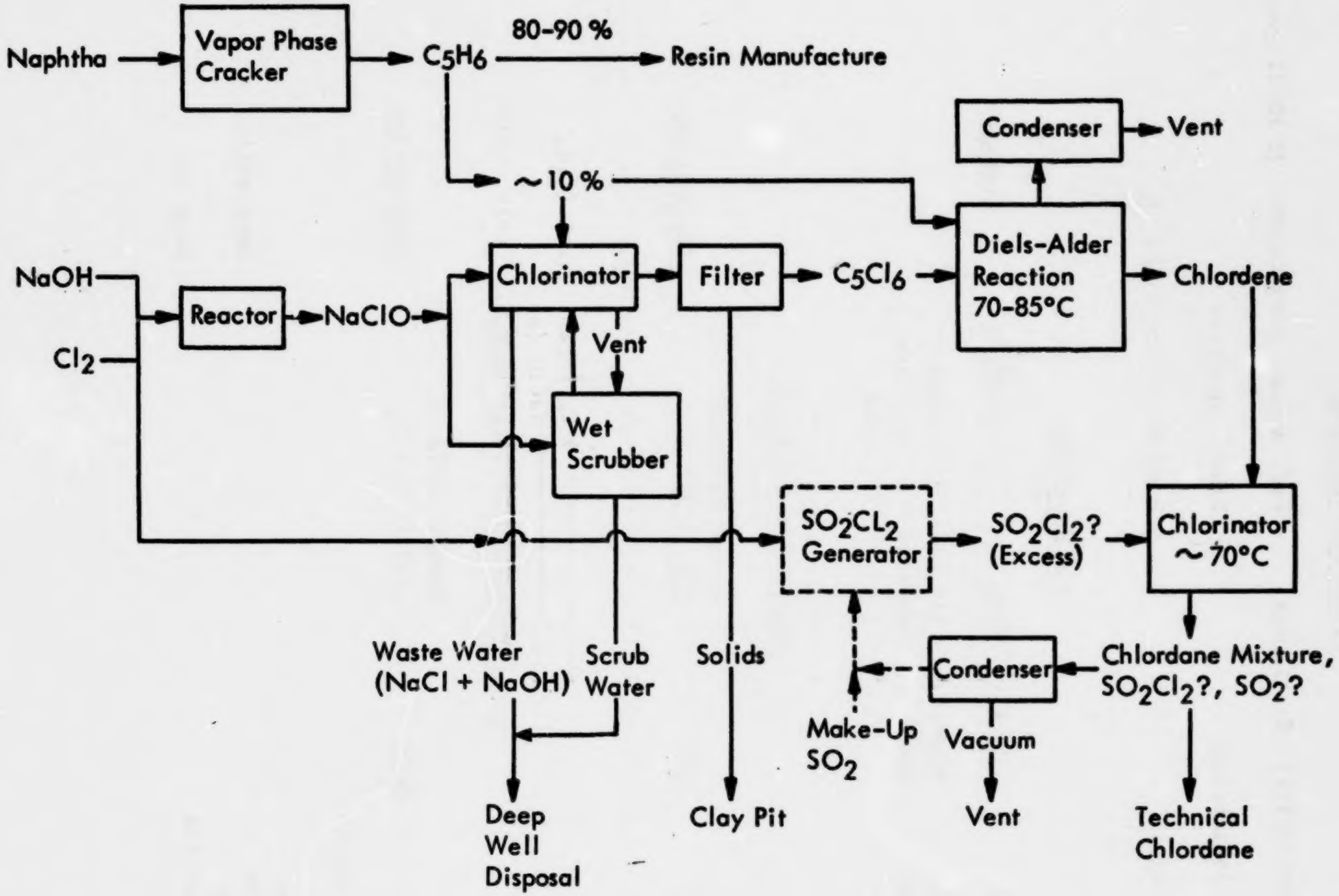

Naphtha
Vapor Phase Cracker
C_5H_6
80-90 %
Resin Manufacture
Condenser
Vent
~10 %
Diels-Alder Reaction 70-85°C
NaOH
Cl$_2$
Reactor
NaClO
Chlorinator
Filter
C_5Cl_6
Chlordene
Vent
Wet Scrubber
SO_2CL_2 Generator
SO_2Cl_2? (Excess)
Chlorinator ~ 70°C
Waste Water (NaCl + NaOH)
Scrub Water
Solids
Condenser
Chlordane Mixture, SO_2Cl_2?, SO_2?
Make-Up SO_2
Vacuum
Deep Well Disposal
Clay Pit
Vent
Technical Chlordane

Figure 21 - Production and Waste Schematic for Chlordane

Production Equipment

Process continuity: Continuous	Est. annual production: 25 MM lb/year
Equipment dedication:	Plant capacity:
Equipment age:	Formulation on site: No

Raw Materials

Material	Received From	Received By	Storage
1. Naphtha	Woodriver, Illinois	Pipeline	
2. Chlorine	Memphis, Tennessee	Tank cars	
3. Caustic	-	Tanks	

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.			
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			
3. All waste liquids			Deep well
4. Filter solids			Clay pit

Disposition of Technical and Formulated Products

Warehouse On-Site	Shipments: Technical Product Container	Technical Product Transportation	Formulated Products Formulation	Formulated Products Container	Formulated Products Transportation
Small amt.	40-50% tanks	Rail and track	None		
	40-50%, 30-gal. drums,	Truck and rail			
	5-gal. drums	-			

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ____ Yes   X No

Pollution control: The spent hypochlorite wastewater has about 2% NaOH and 400 ppm C_5Cl_6. The chlordane production and handling area is diked and all run-off and process wastes go to deep well disposal on the plant site.

The well is state approved and has been in use for 6 years. It goes 2,600 ft deep to a Dolomite (Vugular) layer which is very porous and the discharge does not spread much--perhaps 5 acres in 6 years. The strata already has salt in it. The shaft has three casing. A tube liner containing water at high pressure goes to 2,300 ft and the top 600 ft is further sealed to prevent surface water contamination. Velsicol has a permit for a second well which will go to 6,000 ft, to be completed in December 1971. It will also handle wastes from the resin part of the plant (these contain fluorides) which are presently being discharged. Those wastes have to be monitored for chlordane, for dissolved solids, BOD, etc. Velsicol monitors chlordane, but also has an outside lab check occasionally and the state also checks sometimes--levels are probably below 1-5 ppb, level which would be toxic to fish (LD_{50} = 1 ppb for chlordane; 25-30 ppb for heptachlor). Five companies in Illinois use deep-well disposal. Cost is $40-90/ft.

Chlorine from the Cl_2 tanks is forced out under pressure--no losses--meets Chlorine Institute Specifications. Velsicol is installing automatic shutoffs.

The tank cars are leased, used for chlordane only. Occasionally some are not needed and are returned to railroad company following cleanup with detergent--the wash goes to deep-well disposal. The tank trucks are received clean and dry from the trucking company--make a one-way trip and then are cleaned by the trucker before being sent to the next job. The trucks are self draining and the trucker may use a bucket to catch drips, but he probably cleans the truck with detergent, steam and air and dumps the washings in the sewer.

Drums are lined, open top: filling--no ventilation problems--no controls. Have had drum punctures, rail accidents, but no full truck spills: biggest spill in the last couple of years was three or four drums. Drum (disposal) is the formulators' problem. Recommended cleanup is kerosene wash and detergent wash but they may throw washings on the ground.

Chlordane is very stable and does not degrade in detergent. The half-life in soil is about 2 years (although it does not migrate or biomagnify). The technical material is fairly viscous.

Emergency procedure--send technical assistance as soon as word of spill is received. Recommend clay absorption or rag wipe-up of spill with burial of material at least 12 in. below ground level. Do not recommend absorption on sawdust and burning.

Quality control: Velsicol uses glc to monitor product and to get what they call "fingerprint" chlordane which apparently contains 7-8% heptachlor. Product color can be a bigger problem than composition. Any off-specification materials are easily blended off. Analytical samples are drummed and sold. Drums are inspected for water or liner tears. Have had little if any rejects from formulators--one claim about water content.

Safety and personnel health: Operating personnel are union; new operators come from other parts of the plant by making a bid for an opening in the chlordane unit. (No one has ever bid out of chlordane). New operators get a 15-30 day training period under a chief operator.

A study of 15 employees who had been handling chlordane for a long time found no detrimental health effects: Ind. Med. & Surg., 33 (10), 726-7 (1964). There has been no authenticated loss of life from chlordane, see: "Monograph on Chlordane Toxicological and Pharmacological Properties," Dr. L. Ingle (1965). Workers around the chlorination units have hand, eye, foot protection and standby (Scott) respiratory equipment.

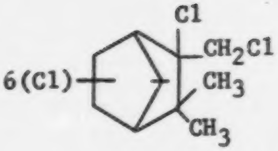
Fires--have plant fire squad; have had no warehouse fires or major plant explosions.

General: Most of the Chlordane is sold to independent formulators, with only a few tank car customers. Velsicol has started formulating only last year and has this done by contractors in Des Moines, Iowa and Napoleon, Ohio. Products are Belt-(clay powder pellets for use on corn)- and Gold Crest-(a 72% solution, 8 lb/gal in petroleum distillate - 10% inert - for use with fertilizer). These are sold through independent stores.

CASE STUDY NO. 5

Pesticide: Toxaphene

Chemical name and formula:


Cl
CH2Cl
6(Cl)
CH3
CH3

Mixed isomers of chlorinated camphene
(67-69% chlorine)

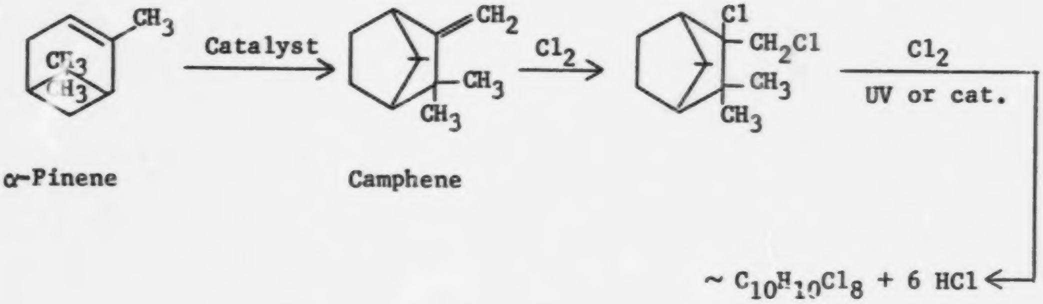
Chemical class: Chlorinated hydrocarbon

Pesticide class: Broad spectrum insecticide

Description: Waxy solid, insoluble in water; moderately toxic; low persistence compared to DDT

Producers: Hercules (Brunswick, Georgia); Sonford Chemical; Strobane-T produced by Tenneco is similar

Production chemistry:


CH3
CH3
CH3
Catalyst
CH2
CH3
CH3
Cl2
Cl
CH2Cl
CH3
CH3
Cl2
UV or cat.
α-Pinene
Camphene
~ C10H10Cl8 + 6 HCl

Toxaphene (mixed isomers
and related compounds
67-69% Cl)

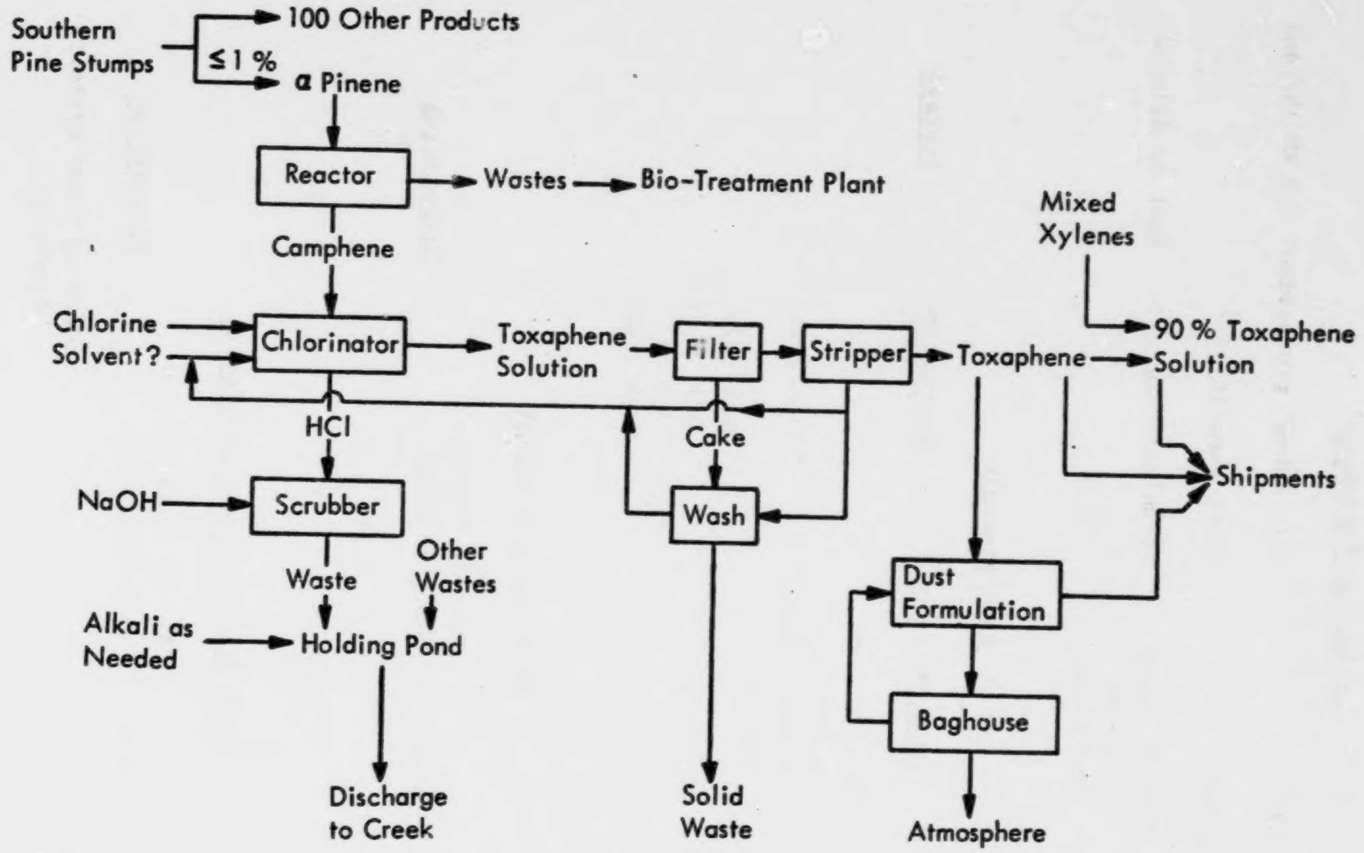

Southern
Pine Stumps
100 Other Products
≤1 %
α Pinene
Reactor
Wastes
Bio-Treatment Plant
Camphene
Chlorine
Solvent?
Chlorinator
Toxaphene
Solution
Filter
Stripper
Toxaphene
Mixed
Xylenes
90 % Toxaphene
Solution
HCl
Cake
Shipments
NaOH
Scrubber
Wash
Waste
Other
Wastes
Alkali as
Needed
Holding Pond
Dust
Formulation
Baghouse
Discharge
to Creek
Solid
Waste
Atmosphere

Figure 22 - Production and Waste Schematic for Toxaphene

Production Equipment

Process continuity:		Est. annual production:	45 MM lb/year
Equipment dedication:		Plant capacity:	
Equipment age:	From 20 years to brand new 1948 plant	Formulation on-site:	Most is diluted

Raw Materials

Material	Received From	Received By	Storage
1. Camphene	On site from α Pinene		
2. Cl_2	Six local (Georgia) sources	Tank cars	
3. Solvent		Tank cars	
4. Clay	(Georgia)	Bulk by rail Tank car	
5. NaOH	(Georgia)	Tank truck	

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. HCl		0.53	
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient	Liquid		Holding ponds system; discharge
2. Solvents			
3. Camphene production	Liquid		Biowaste treatment
4. Waste from scrubbers			Holding pond to creek

Disposition of Technical and Formulated Products

	Shipments				
Warehouse	Technical Product		Formulated Products		
Elsewhere	Container	Transportation	Formulation	Container	Transportation
X	% Small amt., 250-gal galvanized drums	Exported via East cost	% Most, 90% concentrate; 10% xylene	Tanks, 55 Gal, 50-lb, bags pelletized	Rail and truck Exports

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture _X_ Yes ___ No

Pollution control: All liquid effluent from the camphene production step goes to the plant biowaste treatment system. All liquid wastes from the toxaphene unit go to a large holding pond system. This is a new pond system which is about 65% complete; and should be finished in April 1972. The production area is diked so that all liquids go to the holding pond.

Process vents are water, caustic, or lye-scrubbed before venting to the atmosphere. The waste from these scrubbers also goes to the holding pond. The effluent from the holding pond goes to a creek, which goes into the ocean. An "insignificant" amount of toxaphene will be released when this system is put into operation. They have no major problems with leakers or spills. Baghouses are used in the dust concentrate unit, which is located in the toxaphene production area. Dust from the collection system is recycled. There are no scheduled maintenance shutdowns of the complete toxaphene unit. Short shutdowns are made when needed.

The tank cars whether owned by the company or by the railroad are dedicated to toxaphene and are cleaned yearly, with the washings going to the toxaphene recycle system. Tank trucks are customer or truck line owned and are cleaned by them.

Quality control: Technical toxaphene contains 20-30 compounds according to gas chromatographic analysis. Quality control is accomplished by both chlorine content analysis and bioassay. Both must be considered as chlorine content alone does not insure efficacy. There are no impurities that are a particular problem. Off-specification material can generally be reworked with no trouble. Shelf life is excellent.

Personnel and safety: Hercules has rigorous safety standards because of their history in explosives work. They maintain a fire truck and crew on-site. Production workers receive annual checkups and have had an excellent health record with no correlations of death or illness with toxaphene handling.

General: Hercules maintains over 100 aluminum bulk storage tanks at formulator-customer locations. The 90% concentrate is transferred from tanks into these and the formulator draws it out as needed, so that no used drums are generated, and personnel risks are minimized.

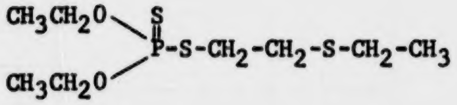
Hercules operates their own emergency aid program to handle spills, although they also belong to the NACA and MCA teams.

Hercules has prepared a 2,500 page report on toxaphene for the Pesticides Regulation Division, Agricultural Research Division (i.e., Federal Register, Vol. 35, No. 148, 31 July 1970).

CASE STUDY NO. 6

Pesticide: Disulfoton (Di-Syston®)

Chemical name and formula:



O-O-Diethyl-S-[2-(ethylthio)-ethyl]phosphorodithioate

Chemical class: Organophosphate

Pesticide class: Systemic insecticide

Description: Liquid of low volatility; insoluble in water; highly toxic; nonpersistent

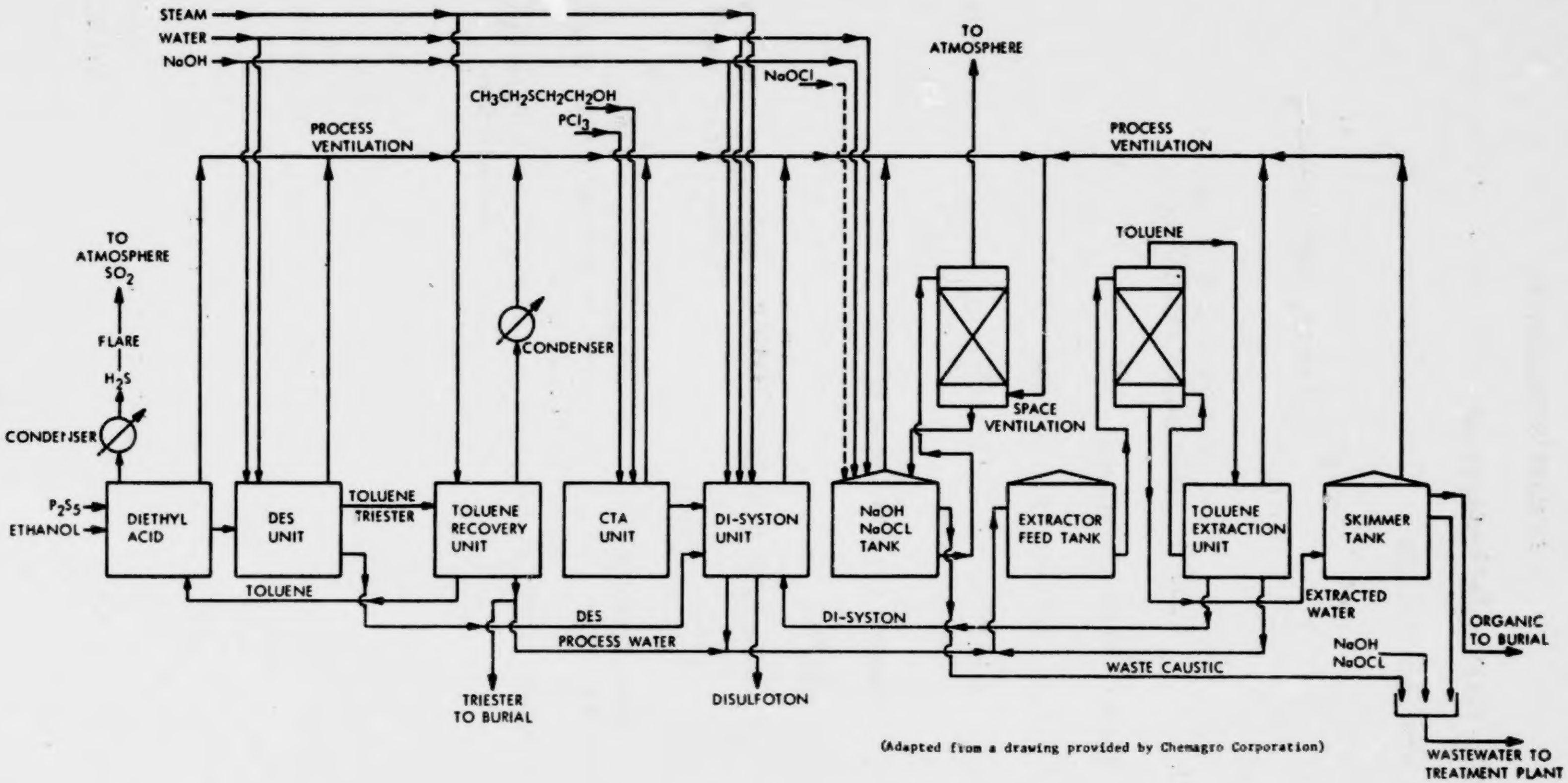
Producers: Chemagro (Kansas City, Missouri)

Production chemistry:

$$P_2S_5 + 4C_2H_5OH + 2NaOH \xrightarrow{\text{Toluene}} \underset{\text{"Diethyl Salt" (DES)}}{2(C_2H_5O)_2P(S)SNa} + H_2S + 2H_2O$$

$$PCl_3 + \underset{\text{"Thio Alcohol"}}{3HOC_2H_4\text{-}S\text{-}C_2H_5} \longrightarrow \underset{\text{"Chloro Thio Alcohol" (CTA)}}{3ClC_2H_4\text{-}S\text{-}C_2H_5} + P(OH)_3$$

$$(C_2H_5O)_2P(S)SNa + ClC_2H_4\text{-}S\text{-}C_2H_5 \longrightarrow \underset{\text{Disulfoton}}{(C_2H_5O)_2P(S)\text{-}S\text{-}C_2H_4\text{-}S\text{-}C_2H_5} + NaCl$$


STEAM
WATER
NaOH
NaOCl
CH3CH2SCH2CH2OH
PCl3
PROCESS VENTILATION
PROCESS VENTILATION
TO ATMOSPHERE
TO ATMOSPHERE SO2
FLARE
H2S
CONDENSER
CONDENSER
P2S5
ETHANOL
DIETHYL ACID
DES UNIT
TOLUENE TRIESTER
TOLUENE RECOVERY UNIT
CTA UNIT
DI-SYSTON UNIT
NaOH NaOCL TANK
EXTRACTOR FEED TANK
TOLUENE EXTRACTION UNIT
SKIMMER TANK
TOLUENE
SPACE VENTILATION
TOLUENE
DES
PROCESS WATER
DI-SYSTON
WASTE CAUSTIC
EXTRACTED WATER
NaOH
NaOCL
ORGANIC TO BURIAL
TRIESTER TO BURIAL
DISULFOTON
WASTEWATER TO TREATMENT PLANT

(Adapted from a drawing provided by Chemagro Corporation)

Figure 23 - Production and Waste Schematic for Disulfoton

Production Equipment

Process continuity: Semicontinuous
Est. Annual Production: 10 MM lb/year
Equipment dedication: One product
Plant capacity:
Equipment age: ~ 15 years
Formulation on site: Yes

Raw Materials

Material	Received From	Received By	Storage
1. P_2S_5		Rail in 5,000 lb tote bins	
2. Ethanol		4,000-5,000 gal. tank trucks	
3. NaOH	Kansas City, Missouri		
4. Ethyl mercapto ethyl alcohol		8-10,000 gal. tank cars	
5. PCl_3		4,000-gal. tank cars	
6. Toluene solvent	Chicago or Houston	8-10,000 gal. tank cars	
7. Sodium hypochlorite			

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. H_2S		0.06	Scrubber and flare
2. $P(OH)_3$		0.075	Wastewater treatment
3. NaCl		0.214	Wastewater

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvent			
3. Other			

Disposition of Technical and Formulated Products

Warehouse On Site	Shipments				
	Technical Product		Formulated Products		
	Container	Transportation	Formulation	Container	Transportation
X (drum)	40%, 55 gal. drums	Mostly truck (some piggy-back)	6 lb/gal E.C. (xylene)	1,30,55-gal. drums	As per technical
			70%, De-odorized	55-Gal. drums	As per technical
			Granular	55-Gal. steel drums	As per technical

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture X Yes ____ No

Pollution control: A new $1.9 million wastewater treatment plant came on stream in June. Caustic conditions (lime) removes some of OPs during retention time of 36 hr. Adjust pH and use polyelectrolyte floculent. Power plant water and sanitary wastes also handled and added. Final effluent is discharged to Blue River--probably has no more than ppm range of any one pesticide now.

Solid waste from treatment plant goes to commercial landfill. Chemagro is planning a biological treatment backup system--possible construction 1973-4.

Process filter cake of diatomaceous earth is decontaminated (N_2 blow; toluene flush (recycle); steam; N_2 blow) then buried. The solids formulation line is well covered by a dust collection system which has a baghouse backed up by a newly installed Venturi-type wet scrubber (alkaline). Formulation equipment cleaned by solvent flush (which is used in next batch) and then by steam and water. Problems: trace emissions of odorants (more in production than in formulation), and disposal of containers. (Est. 2-40 oz liquid left/drum.) H_2S flare and particulates emission from fuel combustion appear to be biggest pollution sources.

Quality control: Di-Syston checked for purity--sometimes must retreat to remove water or unreacted CTA. Impurities may result from poor analysis on intermediate, poor phase separation or equipment failure. Have never had a phytotoxic batch of Di-Syston and no reject batches which could not be reworked or blended off. In one incident disposal of a technical ingredient was necessary: a batch of coumaphos had become contaminated with DDT by an outside formulator and had to be returned and disposed. Incoming drums are spot checked for defects and filled drums are inverted to check for leaks before shipment.

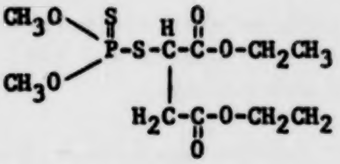
Shelf-life is no problem with Di-Syston--have had no recalls to date. Analytical samples of all products are held in a warehouse several years--will probably recycle eventually.

Personnel health: Workers wear control clothing, boots, gloves, glasses, aprons at times. Have cholinesterase test schedule--every two weeks for production workers and every week for formulators. In addition to the Di-Syston (class B poison) the CTA intermediate is very irritating to skin and eyes. H_2S is toxic. The Filter Cake cleanup (probably once a day) requires extra care--full face mask and respiratory equipment. Have had no fatalities or major injuries, fires or explosions at Chemagro and no small fires with Di-Syston.

CASE STUDY NO. 7

Pesticide: Malathion

Chemical name and formula:



O-O-Dimethylphosphorodithioate of
diethyl mercaptosuccinate

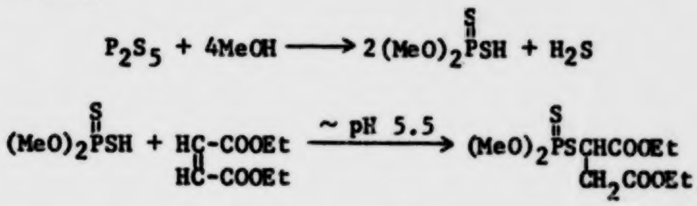
Chemical class: Organophosphate

Pesticide class: Nonsystemic insecticide and acaricide

Description: Liquid of low volatility; slightly soluble in water; low toxicity; nonpersistent

Producers: American Cyanamid (Warners, New Jersey)

Production chemistry:



$$P_2S_5 + 4MeOH \longrightarrow 2(MeO)_2\overset{S}{\overset{\|}{P}}SH + H_2S$$

$$(MeO)_2\overset{S}{\overset{\|}{P}}SH + \begin{matrix} HC\text{-}COOEt \\ \| \\ HC\text{-}COOEt \end{matrix} \xrightarrow{\sim pH\ 5.5} (MeO)_2\overset{S}{\overset{\|}{P}}S\begin{matrix} CHCOOEt \\ | \\ CH_2COOEt \end{matrix}$$

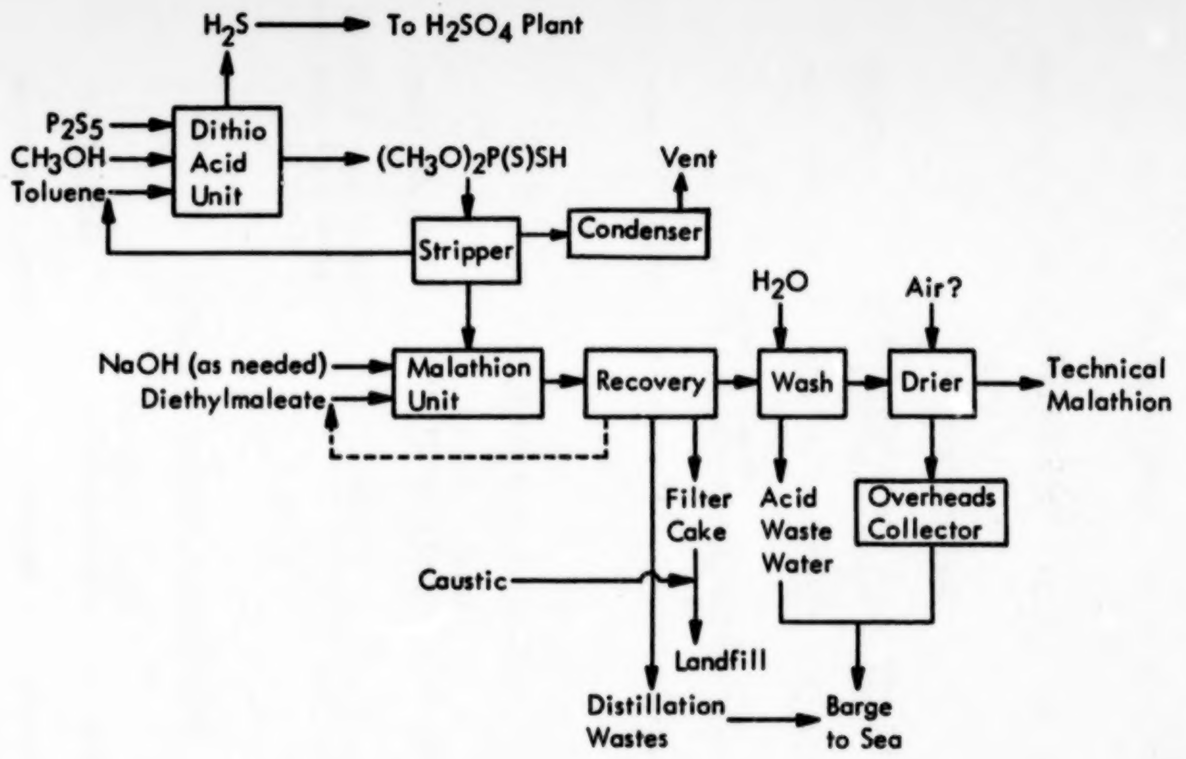

H₂S
To H₂SO₄ Plant
P₂S₅
CH₃OH
Toluene
Dithio Acid Unit
(CH₃O)₂P(S)SH
Vent
Stripper
Condenser
H₂O
Air?
NaOH (as needed)
Diethylmaleate
Malathion Unit
Recovery
Wash
Drier
Technical Malathion
Filter Cake
Acid Waste Water
Overheads Collector
Caustic
Landfill
Distillation Wastes
Barge to Sea

Figure 24 - Production and Waste Schematic for Malathion

Production Equipment

Process continuity: Batch

Est. annual production: 20-25 MM lb/year

Equipment dedication: Other OPs also

Plant capacity:

Equipment age: Est. 15-20 years

Formulation on site: Very little

Raw Materials

Material	Received From	Received By	Storage
1. P_2S_5	Three local sources	Truck, in tote bins	Tote bins
2. MeOH		Rail, tank cars	Bulk
3. Diethyl maleate	Linden, New Jersey	Pipeline	Bulk
4. Toluene	Local		
5. Caustic			

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. H_2S		0.098	Recovered as H_2SO_4 in new plant with good controls
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient	Aqueous	Unknown	Barge to deep sea
2. Solvents toluene	Gaseous	Unknown	Atmosphere
3. Liquid Wastes and spills			To holding pond eventually barged to the sea

Disposition of Technical and Formulated Products

Warehouse Elsewhere	Shipments				
	Technical Product		Formulated Products		
	Container	Transportation	Formulation	Container	Transportation
X (10-12 locations)	10-12%, tanks, 5,30,55-gal. lined drums	Rail and truck	< 5%, production, dust and powder	Drums	Mostly export

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ____Yes _X__NO

Other regulations apply: Federal government regulations apply to sea disposal.

Pollution control: The only by-product of malathion is H_2S, which is recovered as H_2SO_4 in a new sulfur recovery unit. Emissions from this recovery unit meet New Jersey requirements of < 5.5 lb NO_x per ton H_2SO_4 and < 6.5 lb SO_2 per ton H_2SO_4. Some toluene is lost from the malathion distillation process, but emission factors are not known.

The acid production center, which was rebuilt 2 years ago and is used to produce both malathion and phorate, is generally considered to be the most hazardous area of the plant. This unit is completely diked, has separate fire walls, CO_2 blanket system, and no floor drains.

Wash water from the washing process as well as other liquid waste (spills, etc.) go to a holding pond and is eventually barged to sea (150-200 miles out). Cleanup of equipment is limited to once or twice a year when changing products. Waste from this operation is barged to sea. "Extensive" precautions are taken against cross-contamination at this time, and to date they have had no problems. They have been barging their waste to sea for about 4 years.

The only solid wastes generated are filter cartridges. These are decontaminated with NaOH, and are buried with lye in a land fill (on site?). Dust in the formulation area is collected in a baghouse and recycled.

Containers are statistically spot checked before use. Defective lots of containers are rejected. Containers are not pressure checked.

The storage of empty containers before they are used is very important in preventing leakers. Very few complaints about leaks have been received. They try to use the same carriers all the time (rail, truck etc.), and this seems to help. However, LTL shipping has the potential for causing problems because of mixing shipments.

Quality control: AOAC methods are used on raw materials and GLC methods are used on products. No critical impurities are a problem and any off-specification batches can be blended off or easily reworked. Shelf-life of malathion is good, over 2 years. Return of purchased product is not accepted unless special arrangements have been made.

Safety and personnel: Fire and safety practices are standard. The plant has its own fire department which is supplemented by the local fire department. The P_2S_5 venting system is equipped with a CO_2 extinguishment system. The plant area is not systematically diked to catch firewater run off. Some of the bulk storage areas are diked. American Cyanamid has its own 24 hr/day emergency service for malathion and phorate. The phone number is on all containers as well as malathion bulk storage tanks.

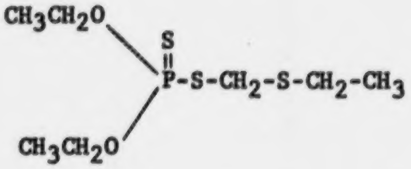
General information: The original plant was constructed during World War I.

The distribution of technical material to formulators in the U. S., as percentages of sales, are: West (15%); Midwest (20%); N.E. (25%); S.E. (20%); and Great Plains (15%). Exports of the technical material go out of New York primarily and are in 55-gal. drums.

CASE STUDY NO. 8

Pesticide: Phorate (Thimet®)

Chemical name and formula:



O,O-Diethyl S-(ethylthio)-methyl phosphorodithioate

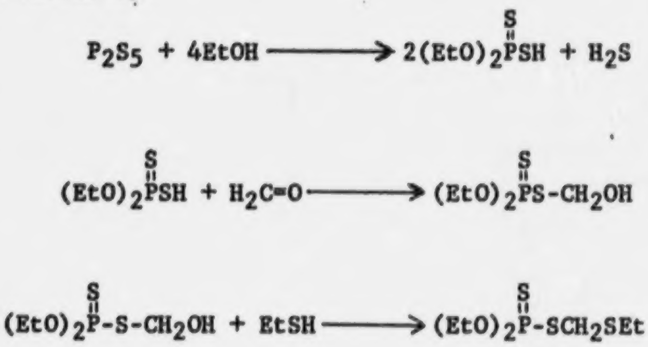
Chemical class: Organophosphate

Pesticide class: Systemic insecticide

Description: Liquid of low volatility; insoluble in water; highly toxic; nonpersistent

Producers: American Cyanimid (Warners, New Jersey)

Production chemistry:



$$P_2S_5 + 4EtOH \longrightarrow 2(EtO)_2\overset{S}{\overset{\|}{P}}SH + H_2S$$

$$(EtO)_2\overset{S}{\overset{\|}{P}}SH + H_2C{=}O \longrightarrow (EtO)_2\overset{S}{\overset{\|}{P}}S\text{-}CH_2OH$$

$$(EtO)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}CH_2OH + EtSH \longrightarrow (EtO)_2\overset{S}{\overset{\|}{P}}\text{-}SCH_2SEt$$

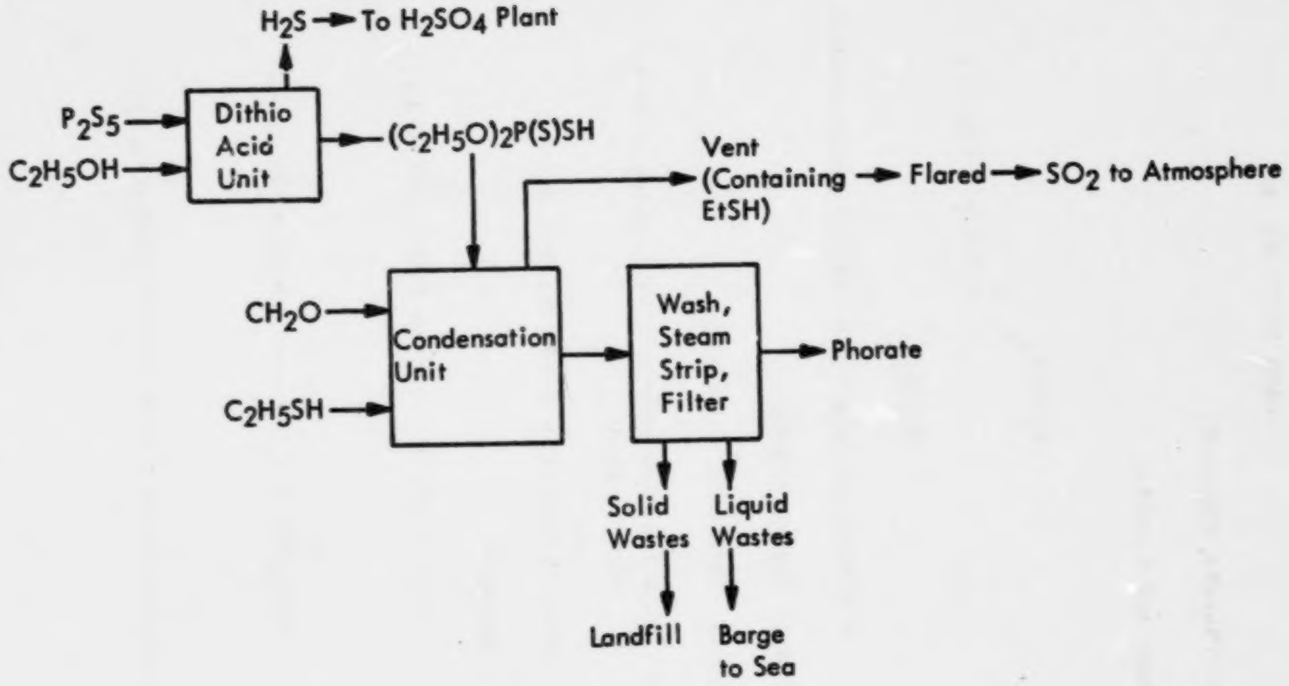

H_2S → To H_2SO_4 Plant
P_2S_5
C_2H_5OH
Dithio Acid Unit
$(C_2H_5O)_2P(S)SH$
Vent (Containing EtSH) → Flared → SO_2 to Atmosphere
CH_2O
C_2H_5SH
Condensation Unit
Wash, Steam Strip, Filter
Phorate
Solid Wastes
Liquid Wastes
Landfill
Barge to Sea

Figure 25 - Production and Waste Schematic for Phorate

Production Equipment

Process continuity:	Batch	Est. annual production:	8 MM lb/year
Equipment dedication:	Part used for other OP's	Plant capacity:	
Equipment age:		Formulation on site:	Very little

Raw Materials

Material	Received From	Received By	Storage
1. P_2S_5	Three local sources	Truck	Tote bins
2. Ethanol	Local services	Tank trucks	
3. Ethyl mercaptan			
4. Formaldehyde			

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. H_2S		0.12	Sulfur recovery to H_2SO_4
2. C_2H_5SH			Burned in a flare

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active Ingredient	Aqueous	Unknown	Barge to deep sea
2. Solvents: toluene	Gaseous	Unknown	Atmosphere
3. Other: Liquid wastes and spills			To holding pond eventually barged to the sea

Disposition of Technical and Formulated Products

Warehouse		Shipments				
		Technical Product		Formulated Products		
On-Site	Elsewhere	Container	Transportation	Formulation	Container	Transportation
X	X	55-gal. Drums	Truck and rail in full loads only	Small amount to E.C. (6 lb/gal)	1-gal. metal cans (4/carton) 5-gal. cans (palletized and strapped)	
				By contract formulators: 50-lb bags 10-lb bags (6/carton) 15-lb bags (4/carton)		

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture _____Yes __X__No

Pollution control: The major by-product is H_2S which is recovered (see malathion). Some ethyl mercaptan is burned and discharged as SO_2 to the atmosphere. Other wastes are handled as those for malathion. Equipment is generally cleaned up once per year at the end of the 6 months or so production run and wastes barged to sea.

Quality control: Mostly GLC methods of analysis. Have recalled a few batches from the contract formulator for reworking. Shelf-life is good--at least a year.

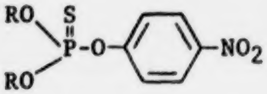
Formulation: Nearly all the phorate goes directly in full car or truck lots to contract formulators where it is formulated to 10-15% granules. American Cyanamid inspects the formulator's facilities at least once a year and requires, in its contract, certification that the formulator will use approved drum handling methods; drums are washed out with caustic-detergent solution, sent to incinerator-type reconditioners, and are not reused for food products. Formulated products are sold in American Cyanamid containers to dealers, co-ops and farmers--perhaps 1,000 outlets in all. Containers are special heat sealed 50-lb bags which have three layers--paper, aluminum and polyethylene.

General: Phorate has agricultural use labels only. Major use areas are: Midwest-Great Plains (60%); West Coast (15%); S.E. (10%); and N.E. (10%); very little export. See also Malathion.

CASE STUDY NOS. 9 AND 10

Pesticide: Parathion and methyl parathion

Chemical name and formula:



O,O-Diethyl O-p-nitrophenyl phosphorothioate

and

O,O-Dimethyl O-p-nitrophenyl phosphorothioate

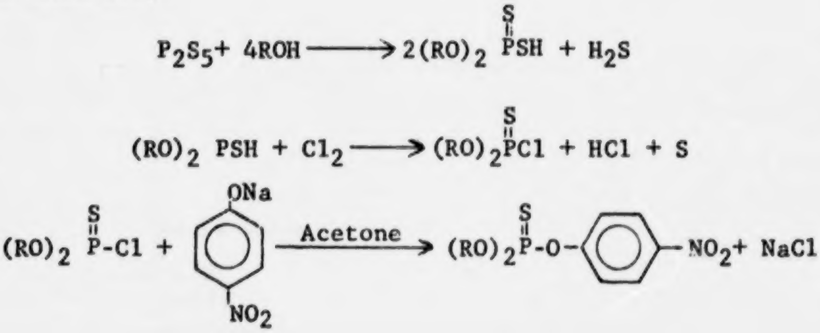
Chemical class: Organophosphate

Pesticide class: Broad-spectrum nonsystemic insecticide

Description: Parathion: liquid of low volatility; insoluble in water; very toxic; nonpersistent.
Methyl parathion: low melting solid (m.p. 36.5°C, low solubility in water; very toxic nonpersistent

Producers: Monsanto (Anniston, Alabama), American Potash, Stauffer, Shell

Production chemistry:



$$P_2S_5 + 4ROH \longrightarrow 2(RO)_2\overset{S}{\overset{\|}{P}}SH + H_2S$$

$$(RO)_2PSH + Cl_2 \longrightarrow (RO)_2\overset{S}{\overset{\|}{P}}Cl + HCl + S$$

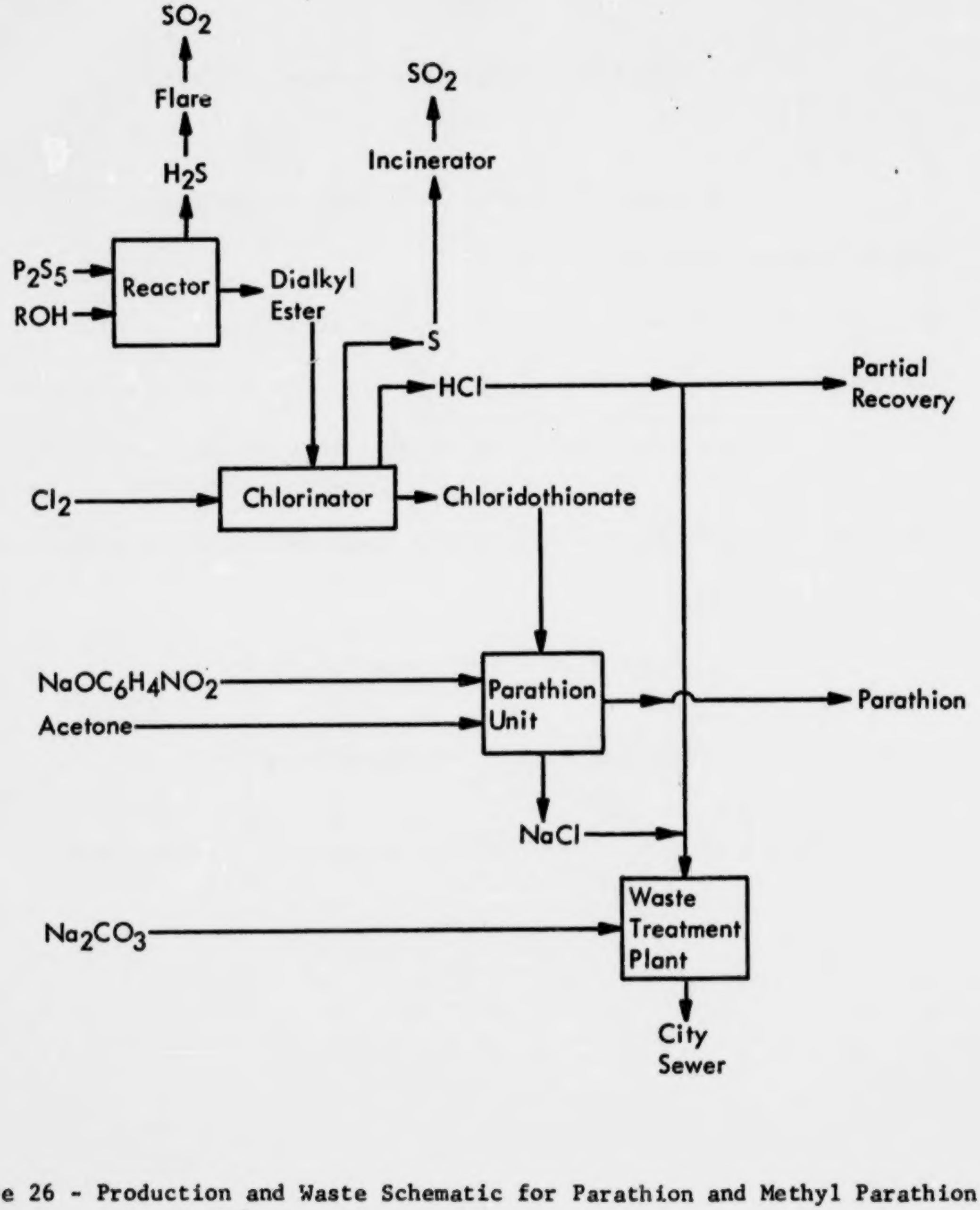

SO2
Flare
H2S
SO2
Incinerator
P2S5
ROH
Reactor
Dialkyl Ester
S
HCl
Partial Recovery
Cl2
Chlorinator
Chloridothionate
NaOC6H4NO2
Acetone
Parathion Unit
Parathion
NaCl
Na2CO3
Waste Treatment Plant
City Sewer

Figure 26 - Production and Waste Schematic for Parathion and Methyl Parathion (Monsanto)

Production Equipment (Monsanto)

Process continuity: Batch

Est. annual production: Ethyl 8 MM and methyl 20 MM lb/year

Equipment dedication: Me and Et parathion

Plant capacity: 55 MM lb/year

Equipment age: 12 years

Formulation on site: < 5% of product

Raw Materials

Material	Received From	Received By	Storage	Remarks
1. P_2S_5	On-site	Tote bins	Tote bins	
2. Cl_2	Louisiana	Rail, tanks	Tank cars	Vented to production system
3. ROH	Louisiana	Rail, tanks		
4. $NaOC_6H_4NO_2$	On-site		Tank	
5. Acetone	Southwest	Rail, tanks		
6. Soda ash	East; middlewest	Rail, tanks	Bulk	For waste disposal

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition	Remarks
1. H_2S	Gas	0.12 calcd.	Flared	SO_2 air pollutant
2. HCl	Gas	0.12 calcd.	Most recycled	Some to liquid waste
3. S		0.11 calcd.	Incinerate	SO_2, some H_3PO_4?
4. NaCL		0.20 calcd.	Biol. waste treatment	Discharged to city sewer

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition	Remarks
Active Ingredient	Aqueous		Liquid waste treatment	< 1 ppm to city sewer
Solvents			Burned	
Other: Organophosphates	Gas liquid		Liquid waste treatment	
p-nitrophenol			Liquid waste treatment	

Disposition of Technical and Formulated Products

Warehouse On-Site	Shipments				
	Technical Product		Formulated Products		
	Container	Transportation	Formulation	Container	Transportation
X	Mostly 55-gal., lined drums, some smaller	~ 90% by truck ~ 10% by rail	< 5% of production	5,30-gal. drums	

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ___X___Yes _______No

Pollution control: Liquid waste, including by-product HCl-NaCl, go to biological treatment facilities, and then into the Anniston sewer system. City specs are for < 1 ppm parathion. They have had no problem complying on all effluent components. By-product H_2S is burned in a flare, and by-product S is burned. Waste solvent is also burned. No solid wastes are produced except sludge from the biological oxidation system, which is "recycled and discharged at a slow rate into the sewer."

Spills within the plant are washed down, and go into the waste treatment system. Spills outside are handled by Monsanto personnel. The frequency of outside spills has been about 8 to 10 per year, including customer problems. Soda ash breaks down the parathions rather quickly, and is used for decontamination.

Equipment clean-up is required only 1 or 2 times per year and presents no major problem.

Quality control: G. C. methods are used. They have had no particular problem with product quality.

Distribution: Most of the production is shipped to warehouses around the country--Monsanto and about 20 carefully selected public warehouses. Monsanto provides technical and safety service to the formulators, about 90% of whom are in the South. Most of the parathions are fomulated as liquids with aromatic solvents. Drums used for the technical material are reused for the formulated products and the formulators try to recycle drums from their customers.

Safety and personnel: Because of the high toxicity of these compounds extensive precautions are taken.[3] Personnel safety record is said to be good. Workers are provided with eye protection, gloves, aprons, disposable overshoes, etc., but not with work clothing. The plant, which was built in 1959, is said to have many safety shutdown features. The only incidents appear to have been small solvent fires.

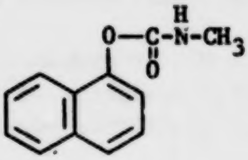
General: Up to 25-30% of Monsanto's production is exported, using Gulf ports. Other major producers of the parathions are Stauffer in Tennessee (capacity of about 30 million pounds per year) and Bayer in Germany.

Monsanto's production is somewhat seasonal, but product shipments are more so. Some of the formulators store between seasons.

CASE STUDY NO. 11

Pesticide: Carbaryl

Chemical name and formula:



1-Naphthyl N-methylcarbamate

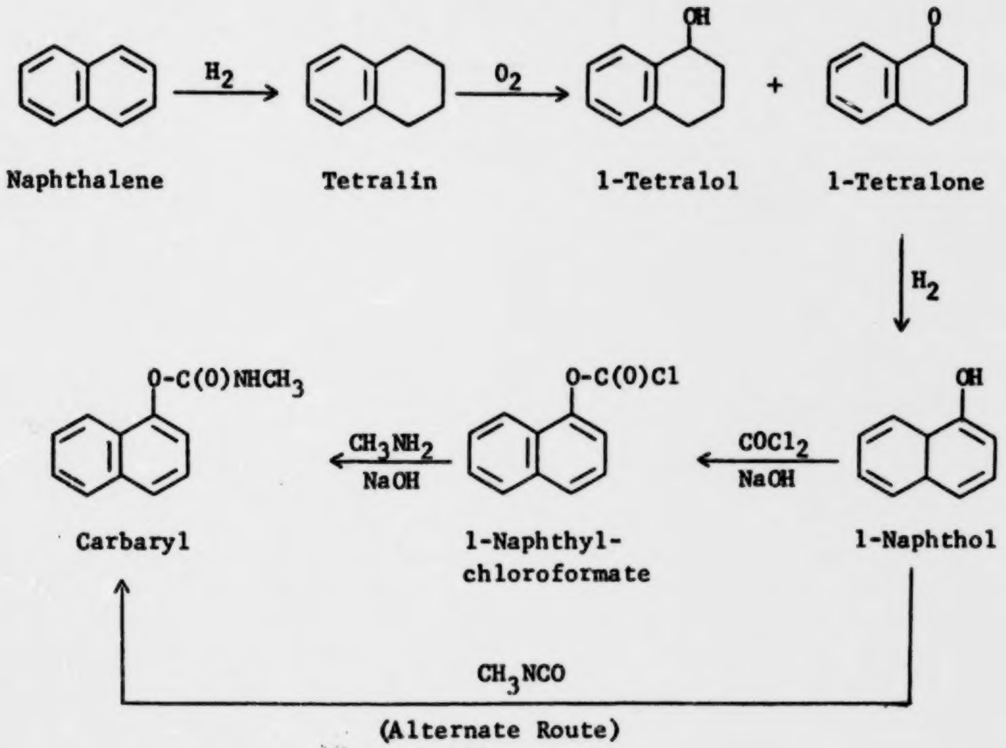
Chemical class: Alkyl carbamate

Pesticide class: Insecticide

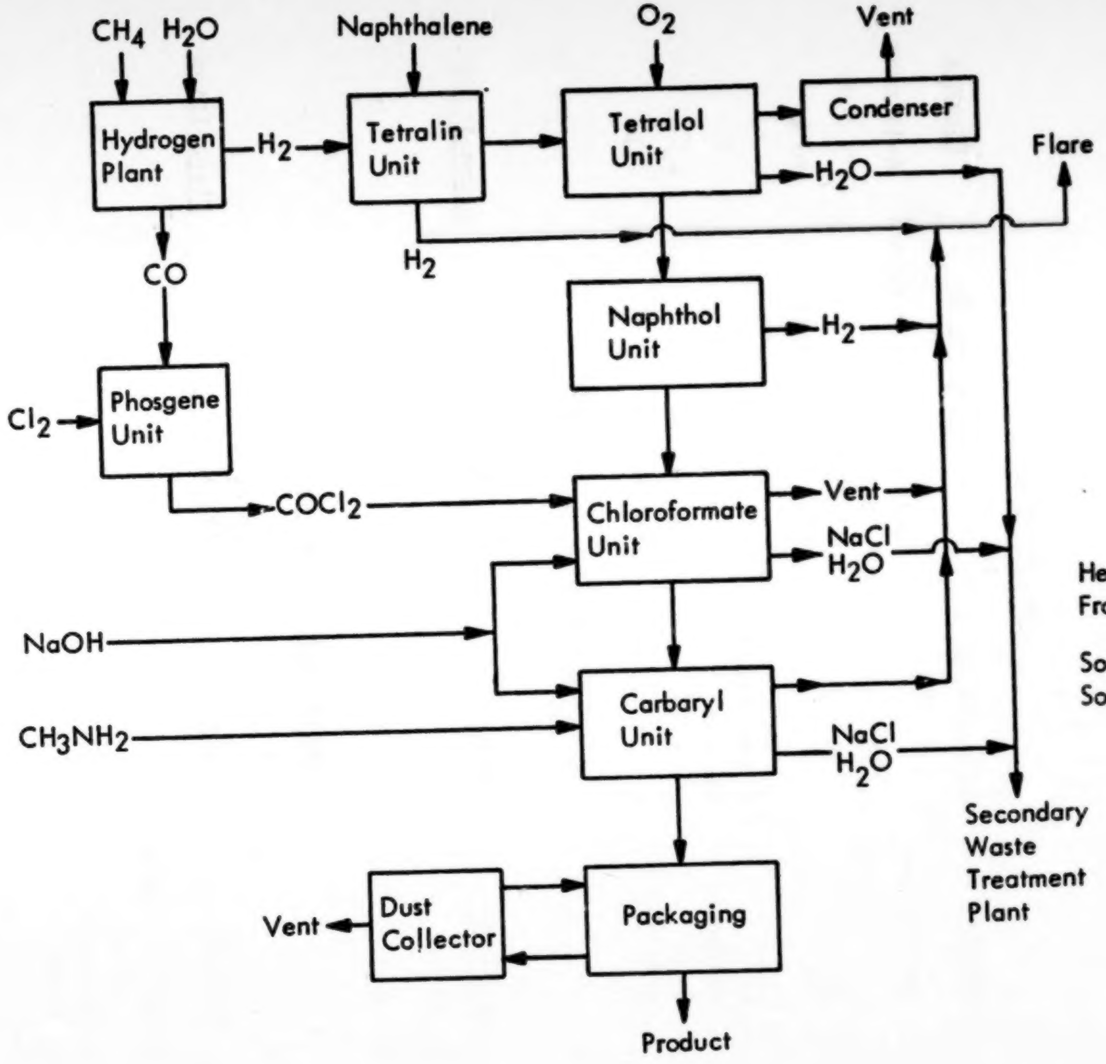
Description: Solid; solubility in water: 99 ppm; moderately toxic; nonpersistent

Producers: Union Carbide (Institute, West Virginia)

Production chemistry:



H2
O2
OH
O
+
Naphthalene
Tetralin
1-Tetralol
1-Tetralone
H2
O-C(O)NHCH3
O-C(O)Cl
OH
CH3NH2
NaOH
COCl2
NaOH
Carbaryl
1-Naphthyl-chloroformate
1-Naphthol
CH3NCO
(Alternate Route)


CH4
H2O
Hydrogen Plant
H2
CO
Naphthalene
Tetralin Unit
H2
O2
Tetralol Unit
Condenser
Vent
H2O
Flare
Naphthol Unit
H2
Cl2
Phosgene Unit
COCl2
Chloroformate Unit
Vent
NaCl H2O
NaOH
CH3NH2
Carbaryl Unit
NaCl H2O
Secondary Waste Treatment Plant
Dust Collector
Vent
Packaging
Product

Heavy Residue From Process → Incinerator

Solvent is Used for Some Steps

Figure 27 - Production and Waste Schematic for Carbaryl

Production Equipment

Process continuity:	Combination batch continuous process	Est. annual production:	18 MM lb/year
Equipment dedication:		Plant capacity:	50 MM lb/year
Equipment age:		Formulation on site:	no

Raw Materials

Material	Received From	Received By	Storage
1. Naphthalene		Dedicated tank cars and barges ~ 90%	Bulk tank
2. H_2		Pipeline	
3. Cl_2		Tank cars, barges 50-90%	Bulk
4. O_2	Linde (local)		
5. Phosgene	On site		
6. CH_3OH		Tank cars	Bulk
7. NaOH (50%)		Barges	Bulk

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.			
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			
3. Other			

Disposition of Technical and Formulated Products

	Shipments				
Warehouse	Technical Product		Formulated Products		
On-Site	Container	Transportation	Formulation	Container	Transportation
~ 50% before export	All, 50-lb bags of 99% AI (palletized)	Mostly rail; some truck and piggyback (full lots only)	By Contract Formulators Most to WP; 2-lb bags (25/baler bag), 5-lb bags (10/bailer bag) Some to liquid; 5-gal. plastic drum (40/pallet)		

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture X Yes ____ No

Pollution control: About 2 lb of chemicals (omitting NaOH and Cl_2) are required to produce 1 lb of carbaryl. By-product wastes are liquid streams, vents and some heavy residues. All process water goes into the plant secondary waste treatment systems. All toxic vents are flared or go to NaOH scrubbers. One nontoxic vent goes to a condenser and then is vented to the atmosphere. Standard hood systems with recycle of recovered material are used in the packaging process.

No solid waste, as such, is generated by Carbaryl production. There is a heavy residue from the process that is burned in an incinerator.

There is one major shutdown per year in the carbaryl unit during the slack season. There are numerous maintenance cleanups of a smaller scale. Washings from these cleanups go into the process waste stream.

Leaks have not been a major problem. Experience with leakers in the 5-gal. plastic drums has been less than 0.1%.

Quality control: Quality control is maintained by using their own analytical methods. There are no critical impurities as such, and any off-specification material can be reworked. Shelf-life is not a problem. Returns have been because of physical inadequacy (lumps, etc.), not AI content. This material can be reworked by the formulator.

Formulation: The technical material goes to about six contract formulators and about 20 customer formulators in the U. S. The contract formulators are under UC control (quality control, production; they package under UC's label).

Safety and personnel: Standard industrial safety equipment is used. All personnel at the plant have escape masks. Work clothes are provided some of the workers, presumably those who work in the most hazardous operations. Work clothes from the insecticide units are bagged and washed separately from the rest of the plant clothes. Cholinesterase tests are routinely run on personnel working in the carbaryl unit.

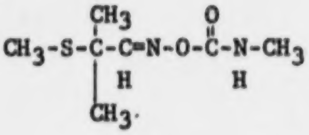
The Institute plant is the regional coordinator for the NACA spill team. They also have a "HELP program" for all chemicals that they produce. The 1972 label will include instructions to burn, not reuse empty bags and plastic containers.

General information: About 50% of the production is exported as technical material primarily through East Coast ports. About 80% of the exported material is shipped in seatainers for convenience and safety. Some formulated material is also exported. The South is the biggest use area; a fairly large quantity goes to the West.

CASE STUDY NO. 12

Pesticide: Aldicarb

Chemical name and formula:



$$CH_3\text{-}S\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}\underset{H}{C}\text{=}N\text{-}O\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}\underset{H}{N}\text{-}CH_3$$

2-Methyl-2-(methylthio)propionaldehyde O-(methylcarbamoyl)oxime

Chemical class: Alkyl carbamate

Pesticide class: Insecticide

Description: Liquid of low volatility; extremely toxic; nonpersistent

Producers: Union Carbide (Institute, West Virginia)

Production chemistry:

$$2(CH_3)_2C{=}CH_2 + 2NaNO_2 + 4HCl \longrightarrow 2NaCl + 2H_2O +$$

$$[ClC(CH_3)_2CH_2NO]_2 \xrightarrow{2CH_3SNa} 2NaCl$$

2-Chloro-2-methyl-1-nitrosopropane dimer

$$+\ CH_3SC(CH_3)_2CH{=}NOH \xrightarrow{CH_3NCO} CH_3SC(CH_3)_2CH{=}NO\text{-}C(O)\text{-}NHCH_3$$

2-Methyl-2(methylthio)-propionaldehyde oxime

Aldicarb

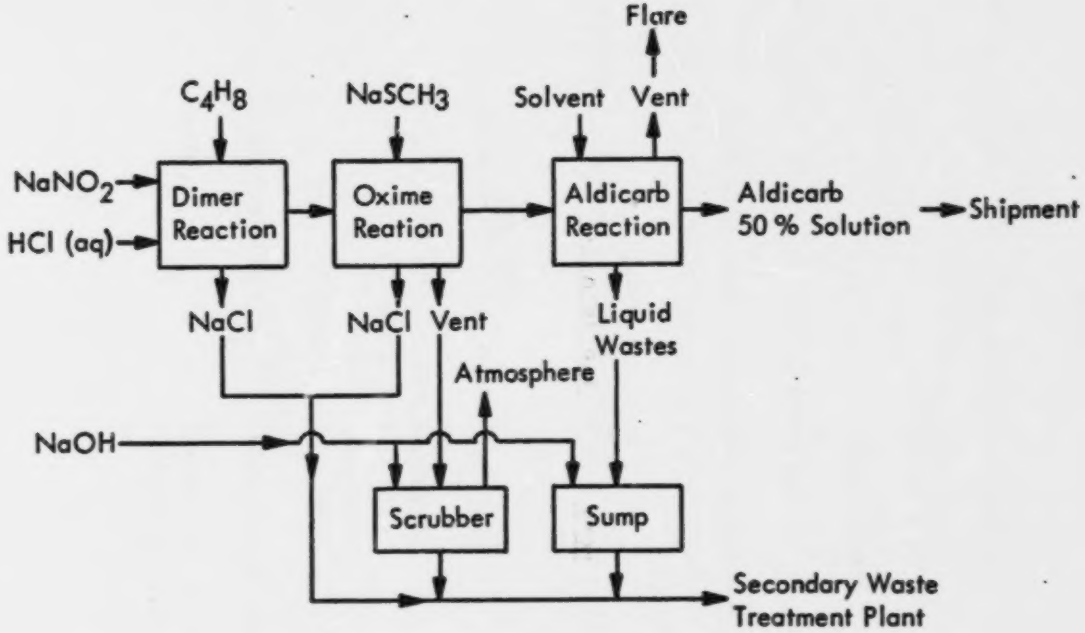

C_4H_8
NaSCH3
Solvent
Vent
Flare
NaNO2
HCl (aq)
Dimer Reaction
Oxime Reation
Aldicarb Reaction
Aldicarb 50 % Solution
Shipment
NaCl
NaCl
Vent
Liquid Wastes
Atmosphere
NaOH
Scrubber
Sump
Secondary Waste Treatment Plant

Figure 28 - Production and Waste Schematic for Aldicarb

Production Equipment

Process continuity: Semi-batch	Est. annual production: 1-3 MM lb/year
Equipment dedication:	Plant capacity:
Equipment age: 15 years	Formulation on site: No

Raw Materials

	Material	Received From	Received By	Storage
1.	$(CH_3)C=CH_2$	East Coast	Tank cars	
2.	$NaNO_2$	East Coast	Tank cars (in solution)	
3.	CH_3SNa	East Coast	Tank cars	
4.	HCl			
5.	CH_3NCO			
6.	Misc. solvents		Tank cars	

Reaction By-Products

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.				
2.				

Other Process Wastes and Losses

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.	Active ingredient			
2.	Solvents			
3.	Other effluent streams			Incinerated or treated

Disposition of Technical and Formulated Products

Warehouse On-Site	Shipments				
	Technical Product		Formulated Products		
	Container	Transportation	Formulation	Container	Transportation
None	All by specially modified tanks	Truck	10% Granules	25-lb bag (2/carton)	Truck and rail

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ___X___ Yes ______ No

Pollution control: All effluent streams from the unit are either incinerated or treated. No solid waste, as such, is generated from aldicarb production. NaCl goes to the liquid waste system. Organic losses are low, about 10 lb per 100 lb Aldicarb, exclusive of solvent loss. Overall, 1 to 2 lb of waste are generated per pound of product. It is anticipated that solvent losses will be significantly improved if a new plant is constructed.

Potentially toxic liquid streams are detoxified (with caustic) before they are sent to the plant waste treatment system. Other potentially toxic effluents are flared. Spills and leakers are handled per "Handling and Safety Guide for Temik 10G."

One reactor in the process is vented to a NaOH scrubber; this waste then goes to the plant waste treatment system. For equipment cleanup steam washout is used in the aldicarb unit for decontamination.

The aldicarb area of the production facilities are diked so that all drainage goes to a caustic sump and then into the plant's secondary waste treatment plant.

The solvent from the technical material is destroyed by flaring at the formulation site.

Formulation: All aldicarb is formulated at one facility several hundred miles from the production site.

The technical material is formulated to a 10% granule on corn cobs (Temik 10G). The formulation goes into DoT 2D bags, which are packaged four to a 12B carton with liner and top and bottom pads. They are currently changing to a two-to-the-carton 25-lb bag. They have had no major problems with packaging. The formulated product is shipped out by both truck and rail shipment.

They have had to repack 3 million pounds of formulation because of bag problems; no spills, however, were involved. Only one layer of packaging failed.

Quality control: Quality control at the AI plant is rather standard. There are no critical impurities of consequence. Quality control at the formulation plant, however, is more difficult than that for Sevin formulation. In some case, off-spec material at the formulation plant must be destroyed.

Safety and personnel: Aldicarb is extremely toxic and atropine is the only antidote. UC does not know of any other industrial chemical process that required comparable safety precautions.

Safety precautions in the production area are highly refined. Wherever there is a possibility of contamination, air suits are worn, e.g., maintenance, decontamination operations. Suits are not required during routine operation. Glove-cabinets are provided at sampling points for toxic streams. ChE's are routinely checked for production personnel.

Safety equipment and procedures at the formulation plant are extensive and are based on care, isolation and diking. The entire formulation plant, which is located in an isolated area, is diked. Workers are supplied with disposable paper overcoverings with taped wrists and legs, boots, and various respiratory devices. Workers in the bagging area wear air suits. They have had some minor problems as the result of operator error, but no serious accidents.

Union Carbide has never had an emergency to date with Aldicarb production or transportation. Temik 10G has been involved in three incidents that UC was aware of:

1. A warehouse fire involving about 100 cases. Water from the fire was diked, UC supervised the cleanup.

2. A small fire set by vandals.

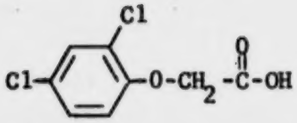
3. A tornado involving about 100 cases in which a warehouse was completely destroyed. It is assumed that the AI in Temik 10G would be destroyed in a fire, because of the corncob rather than clay base.

General information: Union Carbide is the only known producer of Aldicarb. Major uses are on cotton, sugar beets, primarily in the South and West. About 50% of production is exported.

CASE STUDY NO. 13

Pesticide: 2,4-D

Chemical name and formula:


Cl
Cl
O-CH2-C-OH
O

2,4-Dichlorophenoxyacetic acid
(usually as amine salts and esters)

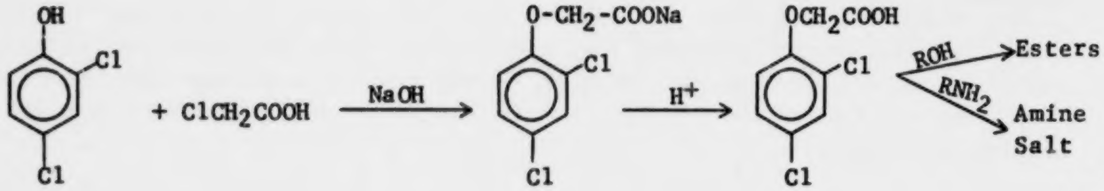
Chemical class: Chlorinated phenoxy

Pesticide class: Herbicide

Description: Solid; salts are water-soluble, acid and esters nearly insoluble; moderately toxic; nonpersistent

Producers: Dow (Midland, Michigan); Chipman (Portland, Oregon)

Production chemistry:


OH
Cl
Cl
+ ClCH2COOH
NaOH
O-CH2-COONa
Cl
Cl
H+
OCH2COOH
Cl
Cl
ROH
Esters
RNH2
Amine Salt

Dichlorophenol | Chloroacetic acid | 2,4-D Sodium salt | 2,4-D

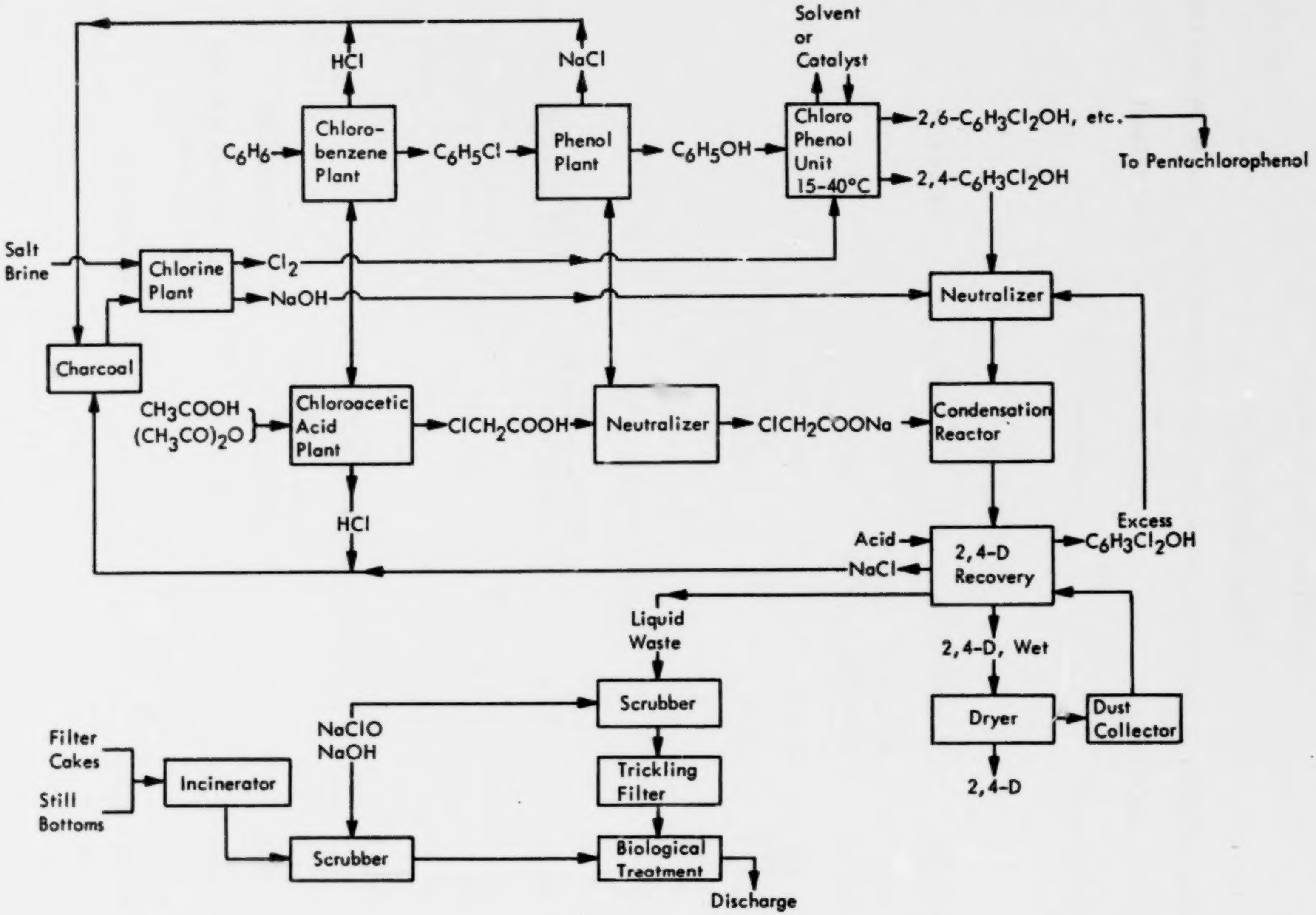

HCl
NaCl
Solvent or Catalyst
C_6H_6
Chloro-benzene Plant
C_6H_5Cl
Phenol Plant
C_6H_5OH
Chloro Phenol Unit 15-40°C
2,6-$C_6H_3Cl_2OH$, etc.
To Pentachlorophenol
2,4-$C_6H_3Cl_2OH$
Salt Brine
Chlorine Plant
Cl_2
NaOH
Neutralizer
Charcoal
CH_3COOH
$(CH_3CO)_2O$
Chloroacetic Acid Plant
$ClCH_2COOH$
Neutralizer
$ClCH_2COONa$
Condensation Reactor
HCl
Acid
NaCl
2,4-D Recovery
Excess $C_6H_3Cl_2OH$
Liquid Waste
2,4-D, Wet
Scrubber
NaClO
NaOH
Dryer
Dust Collector
Filter Cakes
Still Bottoms
Incinerator
Trickling Filter
2,4-D
Scrubber
Biological Treatment
Discharge

Figure 29 - Production and Waste Schematic for 2,4-D (Dow Chemical)

Producer: Dow Chemical

Production Equipment

Process continuity: Semicontinuous	Est. annual production: 35-40 MM lb/year
Equipment dedication:	Plant capacity: 45-50 MM lb/year
Equipment age:	Formulation on site: yes

Raw Materials

Material	Received From	Received By	Storage
1. NaCl	Salt brine wells		
2. Benzene	Bay City, Michigan	Underground pipeline	
3. Acetic acid	South	Rail, aluminum tanks	
4. Acetic anhydride	South	Probably rail, in tanks	

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. HCl, NaCl			Recycle
2. 2,6-D		< 0.01	Convert to C_6H_5OH
3.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient		< 2 lb/day	Lost through air and shoes, etc.
2. Solvents			
3. Filter cakes			Incinerator

Disposition of Technical and Formulated Products

Warehouse On-Site	Shipments: Technical Product[a/] Container	Shipments: Technical Product[a/] Transportation	Shipments: Formulated Products Formulation	Shipments: Formulated Products Container	Shipments: Formulated Products Transportation
X	50% tank cars, drums, bags	Rail	Liquids	Drums and cans	
			Dry	50 lb bags	

---

a/ Includes acid, esters and salts (see text).

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture _X_ Yes ____No

Pollution control: Dow (Midland) is on a very small river and "had to face pollution and housekeeping problems much earlier than others." Have extensive wastewater treatment facilities and huge incinerator equipped with wet scrubber (for chlorinated tars especially). Wastewaters with special contaminants (especially from the tank car wash shed) go through special treatments such as a biologically active trickling filter before going to the general biological treatment plant. Dichlorophenol imparts a taste to water at 0.0005 ppm and kills fish at 2 ppm. A 1968 spill of dichlorophenol plus some 2,4-D caused a fish kill and have since diked around production/storage areas to prevent recurrence. In emergency, a "shot" (holding) pond is automatically switched in.

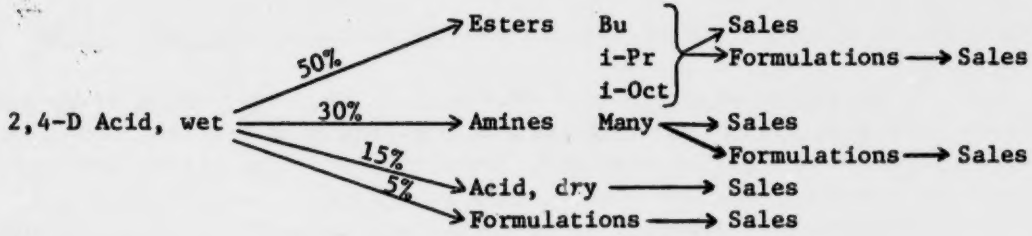
For 2,4-D and 2,4,5-T manufacture nearly all the by-product chloride is recycled (charcoal recovery system) to electrolysis cells. By-product 2,6-D is difficult to degrade biologically and would interfere in waste treatment plant; therefore, it is removed (distillation or otherwise) and converted to pentachlorophenol which has value. (Dow says that a small producer could not afford to do this and also that the 2,6-D may run as high as 12% of product with poor technology.) Other by-products are converted by bleach-oxidation to CO_2, HCl, and removed.

Filter cakes, still bottoms, etc., from 2,4-D and 2,4,5-T production are accumulated and incinerated (1000°C) during the nongrowing season--especially not during April or May.

Dryers are equipped with dust collection. Complete recycle is used. Dow furnishes workers outer clothing, which is washed in in-house laundry with wash water going to waste disposal. Wipe cloths, etc., would also go to laundry or incinerator. Total loss of 2,4-D through air and shoes, etc., is now less than 2 lb/day, although it had previously been as high as 150 lb/day.

Drums used in shipments are one-way; any returns would be incinerated. Tank cars are owned by Dow and are used mostly for herbicides during rush season, but may be used for other Dow chemicals at other times. All are cleaned as needed in a special tank washing shed with detergent and high pressure (see above).

Formulation and packaging: Dow sells 40-60 formulations in addition to technical. The product mix is approximately as follows:



Perhaps 50% of total production is shipped in tank cars (mostly 8,000 gal., some 4,000 gal.) and the remainder in bags and drums. Containers for esters and amines range from tank cars to 5 gal. cans. Formulated products usually go to smaller containers and dry products to 50-lb bags. Over 250,000 5-gal. cans are packaged per year.

Quality control: Use VPC/Computer. Any off-specification material would be treated as required: upgraded, blended, degraded, etc. The tetrachloro dioxin which is a problem in 2,4,5-T production is not a byproduct in 2,4-D production.

Safety and personnel: Fire and occupational safety practices appear to be standard for a large chemical company.

General information: Dow is the major producer (90%) of 2,4-D left since Diamond, Hercules and Monsanto have stopped. Capacity is 45-50 million pounds per year mixed 2,4-D derivatives. Most of the 2,4-D sales are in the grain states. Sales are made primarily through other companies such as AmChem, American Oil, Guth and Farmland Industries. Dow is on the NACA Safety Team, gets approximately one call per week and has compiled a "bible" of information on handling pesticides of all types.

Producer: Chipman

Production Equipment

Process continuity:

Est. annual production: 3-5 MM lb/year

Equipment dedication:

Plant capacity:

Equipment age: 1956

Formulation on site:

Raw Materials

Material	Received From	Received By	Storage
1. Cl_2	Produced on site		
2. Others probably the same as for Dow			
3.			

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Chlorides			Discharge see text
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			See text
2. Solvents			
3. Other			

Disposition of Technical and Formulated Products

	Shipments				
Warehouse	Technical Product		Formulated Products		
On-Site	Container	Transportation	Formulation	Container	Transportation
Some			See text		

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture X Yes ____ No

Pollution control: Over $1 million have been spent for pollution control facilities at this production plant. The wastewater treatment facilities are centered in a continuous flow charcoal absorption plant which is said to reduce phenolics below the 1.0 mg/liter level. (See Figure 30.) Pollution problems from pesticide production is said to be limited to occasional phenolic odor complaints. No area vegetative damage from 2,4-D and no corrosion damage or odor complaints from chlorine has occurred. No landfill of solid wastes is allowed in Oregon. Transportation problems have been apparently few: one incident of leakage by a defective tank car several years ago. Filled drums receive spot check of closures and check in storage. Drum leakers are said to result from rough handling, not defects. Chipman has their own fire department and works with local department. Diking, etc., in the plant area is said to meet insurance requirements. No emergency holding pond appears to exist. Clothing of production personnel probably go to a commercial laundry.

Quality control: No reject batches are made. They have had minimum cross contamination problems. No problem with dioxins.

Distribution: Chipman does not retail 2,4-D. About 50% of production is sold as acid, with formulation done at Portland and outside. Amine salts and the octyl and butyl esters are formulated in Portland, in Chipman facilities in North Kansas City and St. Paul, and by outside formulators. The 2,4-D products are shipped in tanks (rail and truck) down to 1-gal. cans.

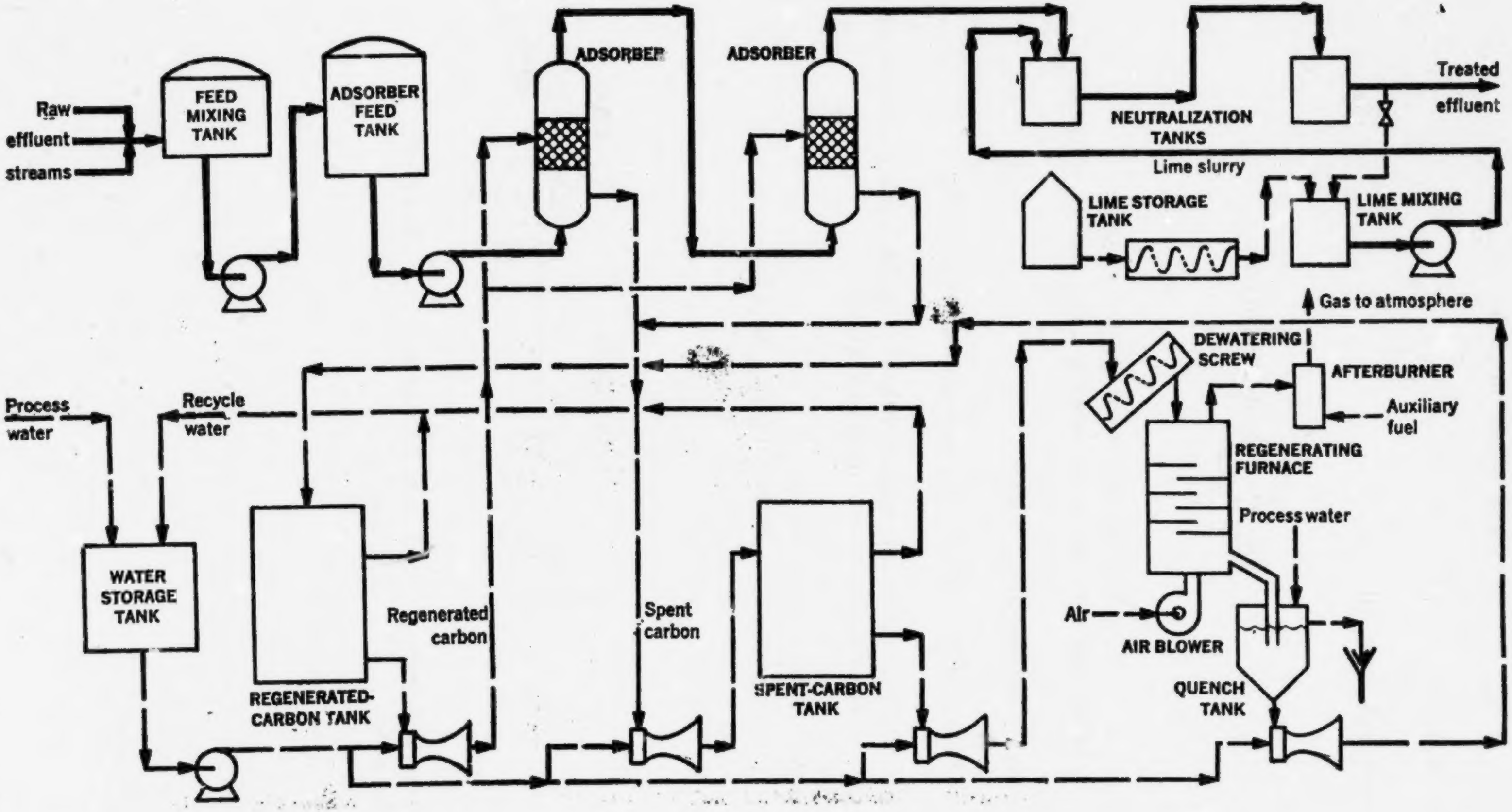
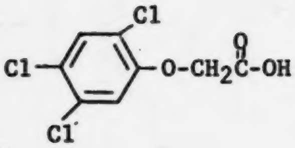

Raw
effluent
streams
FEED MIXING TANK
ADSORBER FEED TANK
ADSORBER
ADSORBER
NEUTRALIZATION TANKS
Treated
effluent
Lime slurry
LIME STORAGE TANK
LIME MIXING TANK
Gas to atmosphere
DEWATERING SCREW
AFTERBURNER
Auxiliary fuel
REGENERATING FURNACE
Process water
Air
AIR BLOWER
QUENCH TANK
Process water
Recycle water
WATER STORAGE TANK
REGENERATED-CARBON TANK
Regenerated carbon
Spent carbon
SPENT-CARBON TANK

Figure 30 - Charcoal Absorption/Filtration Plant for Treating Phenolic Wastes4/

CASE STUDY NO. 14

Pesticide: 2,4,5-T

Chemical name and formula:



2,4,5-Trichlorophenoxyacetic acid
(Also used as amine or sodium salt and as esters.)

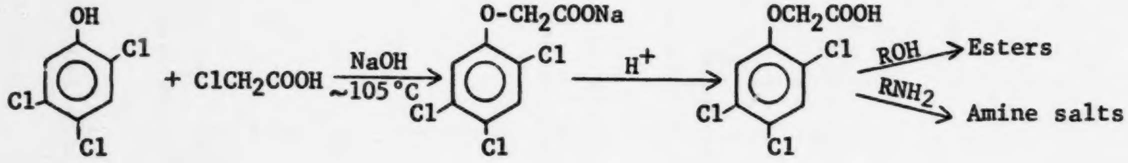
Chemical class: Chlorinated phenoxy

Pesticide class: Herbicide (brush) and growth regulator

Description: Solid; salts are water soluble, acid esters insoluble; moderately toxic; nonpersistent

Producers: Dow (Midland, Michigan)
Thompson-Hayward (Kansas City, Kansas)

Production chemistry:



Trichlorophenol chloroacetic acid — 2,4,5-T, sodium salt — 2,4,5-T

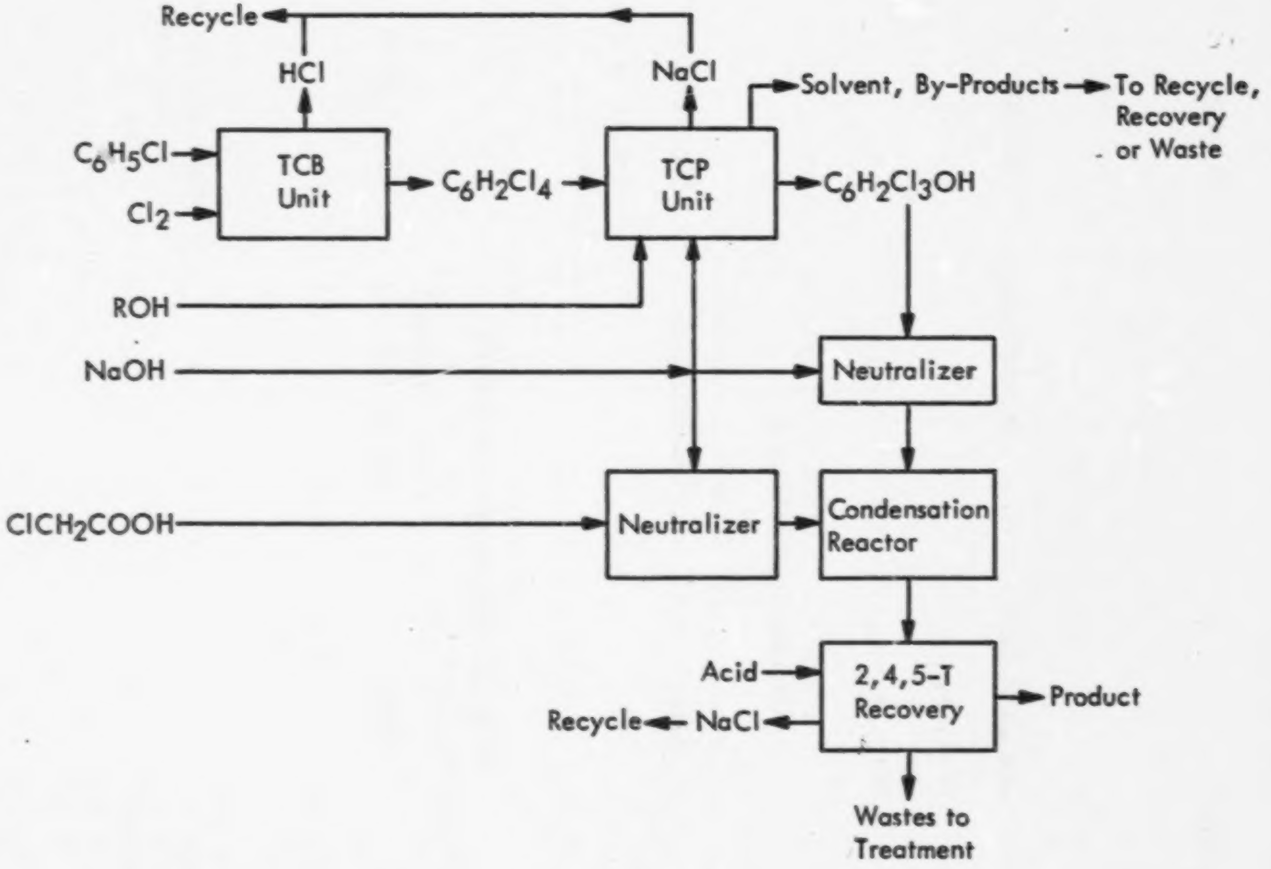

Recycle
HCl
NaCl
C_6H_5Cl
Cl_2
TCB Unit
$C_6H_2Cl_4$
TCP Unit
Solvent, By-Products
To Recycle, Recovery or Waste
$C_6H_2Cl_3OH$
ROH
NaOH
Neutralizer
$ClCH_2COOH$
Neutralizer
Condensation Reactor
Acid
2,4,5-T Recovery
Product
Recycle
NaCl
Wastes to Treatment

Figure 31 - Production and Waste Schematic for 2,4,5-T
(Dow--see Case Study 13 for details)

Producer: Dow

Production Equipment

Process continuity: Semicontinuous	Est. annual production: 3-5 MM lb/year
Equipment dedication:	Plant capacity: 10 MM lb/year
Equipment age:	Formulation on site:

Raw Materials

Material	Received From	Received By	Storage
1. Chorobenzene	On-site		
2. Chlorine	On-site		
3. Chloroacetic acid	On-site		

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. HCl, NaCl			Recycle to Cl_2 unit
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents and by-products			
3. Other: filter cakes, still bottoms incinerated			Recycle, recovery or waste treatment

Disposition of Technical and Formulated Products

Warehouse		Shipments				
		Technical Product		Formulated Products		
On-Site	Else-Where	Container	Transportation	Formulation	Container	Transportation

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture _X_ Yes ______No

Pollution control: See 2,4-D Case History Study No. 13 for details of Dow's waste treatment facilities. The trichlorophenol plant is new and maintains very careful temperature control during the hydrolysis of tetrachloro benzene to avoid the formation of dioxins which can cause chloracne in humans. No chloracne cases have occurred with workers in this plant.

General: Most of the 2,4,5-T is converted to the amine or esters and little is sold as acid. Most of the 2,4,5-T products go to the pasture lands of Texas, etc. Some of the trichlorophenol is sold for direct pesticidal use and some for other uses.

Producer: Thompson-Hayward

Thompson-Hayward produces only the isooctylester of 2,4,5-T and does not isolate the acid in its process.

Production Equipment

Process continuity:	Est. annual production: 2.5-4 MM lb/year ester
Equipment dedication: One product	Plant capacity: ~ 5 MM lb/year (est.)
Equipment age: 10 years	Formulation on site: Yes

Raw Materials

	Material	Received From	Received By	Storage
1.	$Cl_3C_6H_2OH$	Michigan		
2.	$ClCH_2COOH$	Various sources		
3.	NaOH	Various sources		
4.	Isooctyl alcohol	Various sources		

Reaction By-Products

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.	Salt		0.2 lb/lb ester	Oxidation pond, then discharge
2.				

Other Process Wastes and Losses

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.	Active ingredient			
2.	Solvents	Liquid		Sewer
3.	Other mixed phenolic wastes		50-75 lb/month	Commercial landfill
4.	Solid wastes			Landfill

Disposition of Technical and Formulated Products

Warehouse On-site	Shipments: Technical Product: Container	Shipments: Technical Product: Transportation	Shipments: Formulated Products: Formulation	Shipments: Formulated Products: Container	Shipments: Formulated Products: Transportation
X	Very little		Isooctyl ester in xylene-type solvent	55-gal. drums 30-gal. drums 5-gal. drums 1-gal. can (all lined)	Mostly trucks, some rail to West Coast

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ___X___Yes _______No

During production most items are recycled; some of the alcohol goes to the steam condenser and then to the sewer. The biggest problem is disposal of salt. Their liquid waste treatment system is in the process of modification. An "oxidation pond" presently catches all process, service and surface waters, i.e., it receives some pesticides, detergents, spill residues, etc. Periodically the pond level is partially lowered by pumping water over the levee into the Kaw River. In a new system (under construction, ~ \$100,000) the clean-water streams (boilers, etc.) are being separated from waste streams and will go directly to the river. The waste streams will go to the oxidation pond, then to a chemical treatment basin (acid or caustic) and then via city sewer to the river. During equipment cleanup solvent is recycled to the next batch. They usually use the same process and formulation equipment for one product. If the product is changed they would preclean with solvent which would be recycled; then steam clean with condensate going to the sewer; clean with caustic which detoxifies 2,4-D and rinse. Solid wastes go to a landfill; purge of 2,4,5-T units give 50-75 lb/month of mixed phenolic wastes which go to a commercial landfill. They have had little problem from air pollution, but some phenolics are troublesome because of odor (detectable at 0.005 ppm). They are collected by wet scrubber and discharged; also use wet scrubbers if they make the amine salts.

Accidents--a truck once dropped a trailer and broke containers. Cleanup consisted of absorption with clay and burial in landfill. Mixed lots of shipments on trucks are problems if breakage occurs.

Quality control: Use gas chromatography, but do not have much fluctuation. Dioxin impurity of 0.5 ppm in finished product. (T-H process gives only one significant dioxin impurity). In general, little trouble with

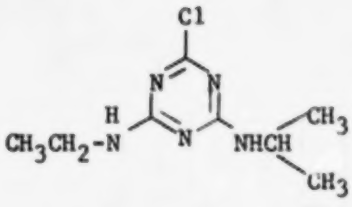
with off-spec 2,4,5-T. A problem batch would be blended off. They keep herbicides well separated from insecticides in warehousing to avoid cross-contamination by the volatile esters.

General: Most of the 2,4,5-T goes to brushy regions of the southwest, rangeland and also to south and southeast.

CASE STUDY NO. 15

Pesticide: Atrazine

Chemical name and formula:


Cl
N
N
H
CH3CH2-N
N
NHCH
CH3
CH3

2-Chloro-4-ethylamino-6-iso-
propylamino-s-triazine

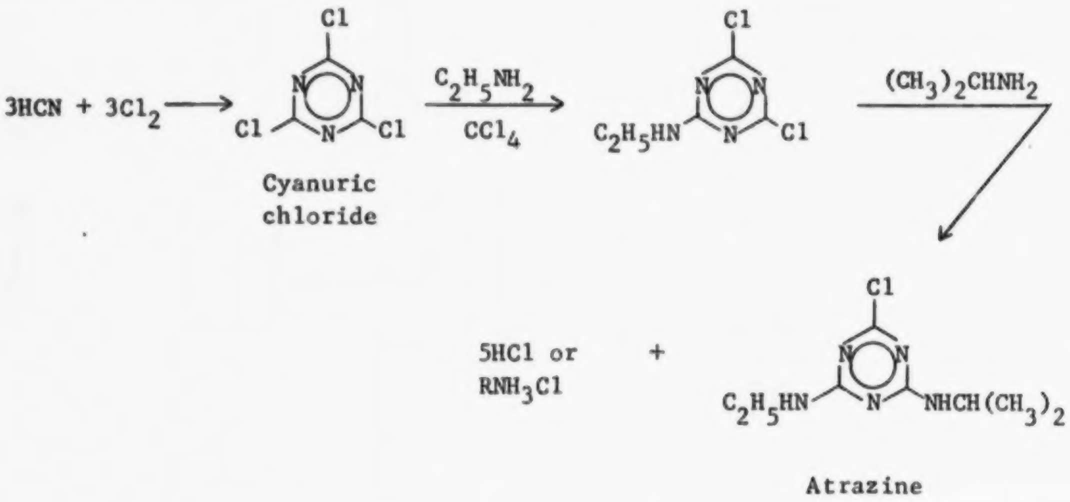
Chemical class: Triazine

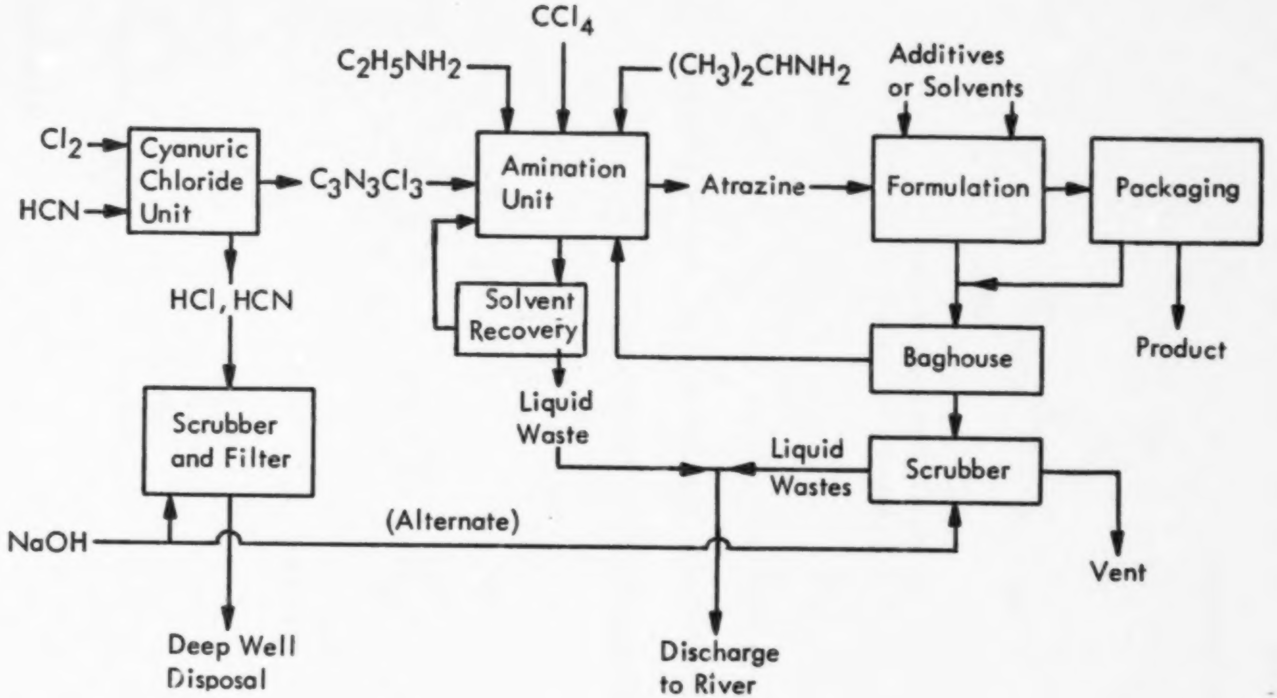
Pesticide class: Selective herbicide

Description: Solid; nearly insoluble in water; low toxicity; nonpersistent

Producers: Geigy (St. Gabriel, Louisiana)

Production chemistry:


3HCN + 3Cl2
Cl
N
N
Cl
N
Cl
Cyanuric chloride
C2H5NH2
CCl4
Cl
C2H5HN
N
Cl
(CH3)2CHNH2
5HCl or RNH3Cl
+
Cl
C2H5HN
N
NHCH(CH3)2
Atrazine



Cl_2
HCN
Cyanuric Chloride Unit
$C_3N_3Cl_3$
HCl, HCN
Scrubber and Filter
NaOH
Deep Well Disposal
$C_2H_5NH_2$
CCl_4
$(CH_3)_2CHNH_2$
Amination Unit
Solvent Recovery
Liquid Waste
(Alternate)
Atrazine
Additives or Solvents
Formulation
Packaging
Product
Baghouse
Scrubber
Liquid Wastes
Vent
Discharge to River

Figure 32 - Production and Waste Schematic for Atrazine

Production Equipment

Process continuity: Continuous

Est. annual production: 100 MM lb/year

Equipment dedication: Mostly atrazine, some other triazines

Plant capacity: 100-150 MM lb/year

Equipment age: 1970

Formulation on site: Yes

Raw Materials

Material	Received From	Received By	Storage
1. HCN	Memphis, Tennessee	Tank cars	Tank
2. "Appropriate" amines	Taft, Louisiana	Tank cars	Tank
3. Cl_2	Adjacent plant	Pipeline	Not stored
4. NaOH			

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. HCl		0.333	Scrubber, then deep well or river
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			
3. Solid waste			Landfill
4. Liquid			River

Disposition of Technical and Formulated Products

Warehouse		Shipments				
		Technical Product		Formulated Products		
On-Site	Else-Where	Container	Transportation	Formulation	Container	Transportation
None	Public warehousing		Rail	% W.P. (80% A.I.)	5-lb bags (multiwalled) (10 per case)	Rail
				Liquid (4 lb/gal.)	1,5 gal. plastic	

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture X Yes ____ No

Pollution control: About 1 lb of effluent is generated per pound of atrazine produced--mostly NaCl. Liquid wastes from the cyanuric chloride production unit ordinarily go to a 6000 ft deep well disposal, after receiving a preliminary polishing (pH adjustment and filtration). The larger amount of liquid wastes from the remainder of the plant are discharged to the river. Sanitary wastes from the plant are chlorinated before they are discharged. The BOD of the waste going to the river is 500 lb/day at the 100 million pound per year production rate.

Solid waste is primarily bag wrappers, car lining material, etc. This waste is disposed of by a commercial operator by landfill not located on the plant site. The formulation and packaging areas are controlled by baghouses and wet scrubbers and atmospheric monitors are used. Losses are said to be substantially < 1%.

Breakage and leakers have not been a major problem. Returns have been < 1%. Overall repackaging is < 2%. Industrial average is said to be 4-5% (for wettable powders?).

Package disposal is a problem. They can be burned, but what happens to the atrazine is not known.

Within the next 2 years, an additional investment equal to 10% of the new plant's cost will be made for spill protection and the treatment of organic waste. Fifty percent of the next 5 years capital budget will be for environmental control.

They may have to consider chlorine recovery instead of deep well in the future, although Louisiana encourages the use of deep wells for waste disposal, and 20 wells within 4 miles of the atrazine plant have operated for over 10 years without major difficulty.

Quality control: Product quality is maintained by "more than 50" on-stream control devices. To date the new plant has never produced off-specification material. Because of the sophisticated control equipment, product yield has been much higher than that of the old plant. Off-specification material could be recycled to be reworked.

Safety: Safety at the St. Gabriel plant is standard for toxic chemical production (HCN handling facilities). Standard emergency equipment is available. Work clothes are provided.

General information: The new plant at St. Gabriel replaces a previous Geigy atrazine plant built in 1959 at McIntosh, Alabama, which was a batch or semibatch operation. The new plant was designed primarily for atrazine (although other triazines can be produced in the same equipment) and production, formulation, and packaging are done in one continuous operation.

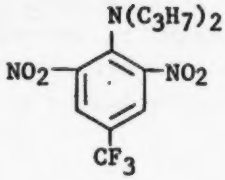
Some atrazine is exported; 2 million pounds was exported last year. Apparently atrazine is also produced by Geigy overseas.

The major uses for atrazine is corn; some is used on sorghum; very little is used by industry (< 10%).

CASE STUDY NO. 16

Pesticide: Trifluralin

Chemical name and formula:


N(C3H7)2
NO2
NO2
CF3

α,α,α-Trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine

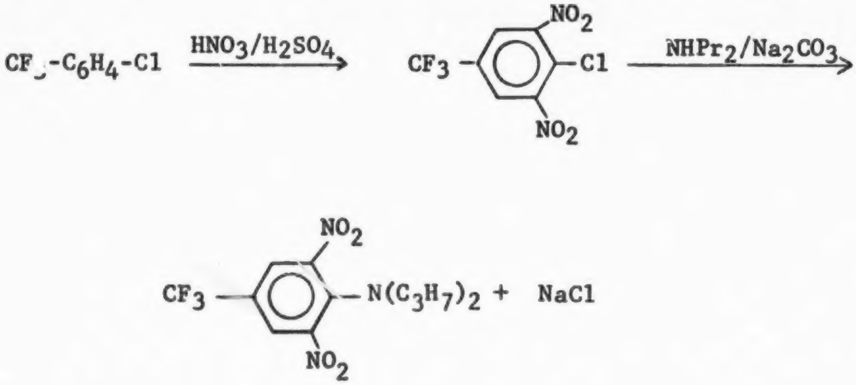
Chemical class: Nitroaromatic

Pesticide class: Selective herbicide

Description: Low melting solid of low volatility and water-solubility; very low toxicity; nonpersistent

Producers: Eli Lilly and Company (Lafayette, Indiana)

Production chemistry:


CF3-C6H4-Cl
HNO3/H2SO4
CF3
NO2
Cl
NO2
NHPr2/Na2CO3
NO2
CF3
N(C3H7)2 + NaCl
NO2

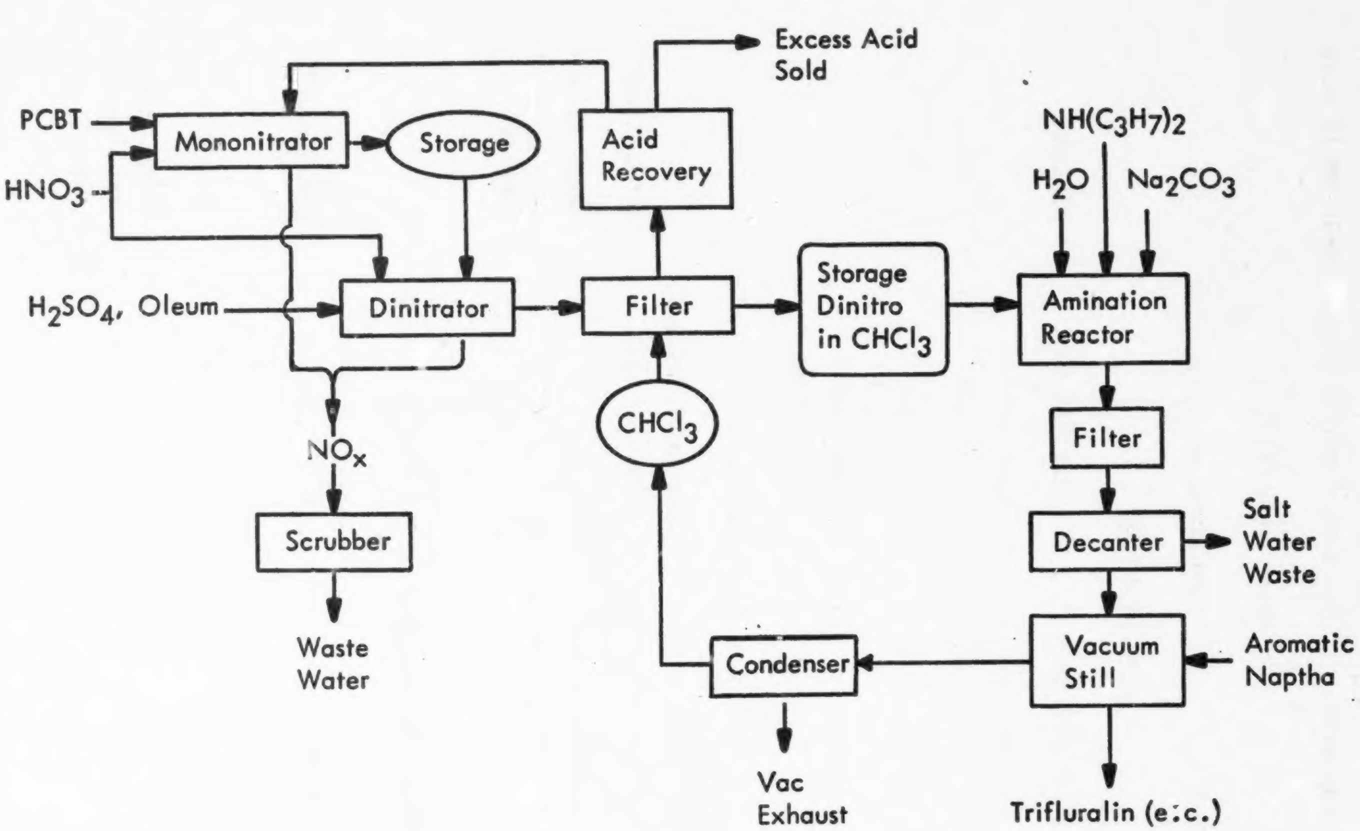

Excess Acid Sold
PCBT
Mononitrator
Storage
Acid Recovery
HNO3
$NH(C_3H_7)_2$
H_2O
Na_2CO_3
H_2SO_4, Oleum
Dinitrator
Filter
Storage Dinitro in $CHCl_3$
Amination Reactor
NO_x
$CHCl_3$
Filter
Scrubber
Decanter
Salt Water Waste
Waste Water
Condenser
Vacuum Still
Aromatic Naptha
Vac Exhaust
Trifluralin (e:c.)

Figure 33 - Production and Waste Schematic for Trifluralin

Production Equipment

Process continuity: Continuous

Est. annual production: 10-20 MM lb/year

Equipment dedication:

Plant capacity:

Equipment age: < 15 years

Formulation on site: Yes

Raw Materials

	Material	Received From	Received By	Storage
1.	PCBT	Buffalo, Chicago	Tank cars	
2.	Diisopropylamine	Various suppliers	Tank cars	
3.	Nitric acid		Tank cars	
4.	Sulfuric acid		Tank cars	
5.	20% Oleum		Tank cars	
6.	Sodium carbanate		100-lb bags	

Reaction By-Products

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.	NaCl	Aqueous	0.17	Waste treatment and discharge
2.				

Other Process Wastes and Losses

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.	Active ingredient			
2.	Solvents			
3.	Liquid waste			Waste treatment and discharge

Disposition of Technical and Formulated Products

	Shipments				
Warehouse Elsewhere	Technical Product		Formulated Products		
	Container	Transportation	Formulation	Container	Transportation
Owned or leased warehouses	Small percentage		Liquid (4 lb/gal.) in aromatic naphtha	5-gal. lined cans metal quarts	
			By contract formulators granules (2.5% A.I. or clay) (< 1% of sales)		

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture __X__ Yes ______ No

Pollution control: NaCl and process water to waste disposal; NO_x to scrubber; H_2SO_4 upgraded and sold; no solid wastes from treflan.

The biological waste disposal plant services all of Lafayette facility, but treflan unit effluent constitues a significant (20-40% ?) part of total. Plant is \$8-10 M investment with operating costs of ~ \$2 M/year. It uses neutralization, settling, aeration and biological. Plant is state approved (the Indiana Stream Pollution Board is very strict). The discharge is cleaner than river water and contains no treflan. Lilly has had no fish kills. The fate of the fluoride in degradation of treflan was unknown. (A new Lilly plant at Clinton handles each waste stream at its source in-plant.)

Leakers--only a few problems. They use corrugated layers between cans and strapped pallets for shipment. Treflan has bright yellow color which makes leaks obvious.

Most of the trifluralin produced is formulated directly at Lafayette as liquids. Liquid formulation and filling equipment used only for trifluralin. The contract formulators of the small amount of granules have no dust problem.

Quality control: Have own specifications and assay on raw materials, use G.C. in process and on final product, approximately no off-specification batches and few impurity problems. They make statistical check of incoming cans before filling. No shelf-life problems; probably > 5 years.

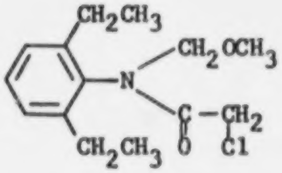
Safety and personnel health: Personnel do not need protective clothing for working with trifluralin. Nitration and dinitro units are watched carefully--have had no explosions.

General: About 10% of production is sent as technical to overseas Lilly subsidiaries and a small amount (<< 5%) is sold to the home and garden market. Most of sales are to dealers, but some goes directly to farmers. Use pattern is ~ 60% on soybeans; ~ 30% on cotton; and ~ 10% all other.

CASE STUDY NO. 17

Pesticide: Alachlor

Chemical name and formula:


CH_2CH_3
CH_2OCH_3
N
C
O
CH_2
Cl
CH_2CH_3

2-Chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide

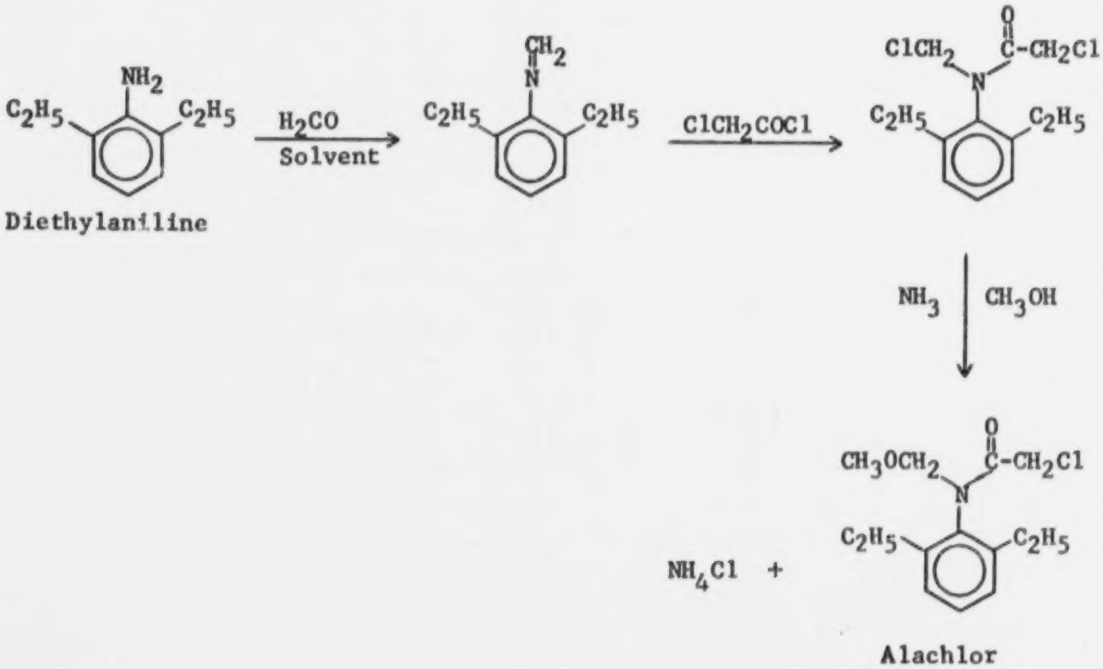
Chemical class: Acetanilide

Pesticide class: Selective herbicide

Description: Low melting (40°C) solid; solubility in water, 140 ppm; moderately low toxicity; skin irritant; nonpersistent

Producers: Monsanto (Muscatine, Iowa)

Production chemistry:


NH_2
C_2H_5
C_2H_5
Diethylaniline
H_2CO
Solvent
CH_2
N
C_2H_5
C_2H_5
$ClCH_2COCl$
O
$ClCH_2$
$C-CH_2Cl$
N
C_2H_5
C_2H_5
NH_3
CH_3OH
O
CH_3OCH_2
$C-CH_2Cl$
N
C_2H_5
C_2H_5
NH_4Cl +
Alachlor

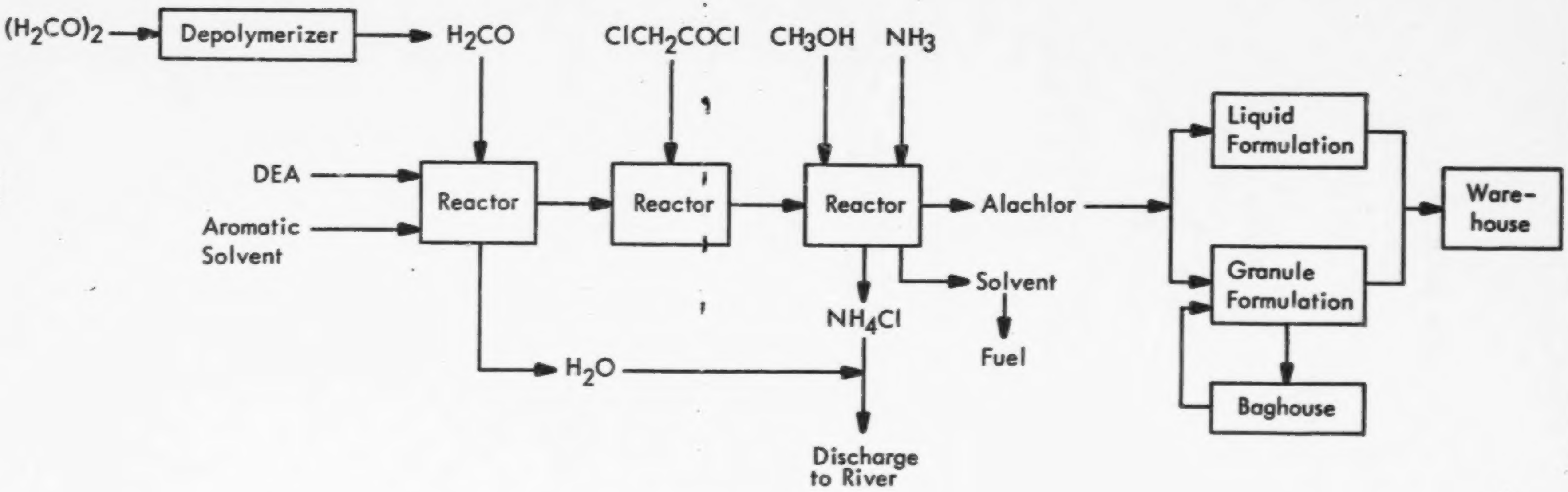

$(H_2CO)_2$
Depolymerizer
H_2CO
DEA
Aromatic Solvent
Reactor
$ClCH_2COCl$
Reactor
CH_3OH
NH_3
Reactor
Alachlor
Solvent
Fuel
NH_4Cl
H_2O
Discharge to River
Liquid Formulation
Granule Formulation
Baghouse
Ware-house

Figure 34 - Production and Waste Schematic for Alachlor

Production Equipment

Process continuity: Batch

Est. annual production: 20 MM lb/year

Equipment dedication: Only this product?

Plant capacity:

Equipment age:

Formulation on site: Yes

Raw Materials

Material	Received From	Received By	Storage
1. 2,6-Diethyl aniline	Southeast	Tank cars	
2. $ClCH_2COCl$	Northeast	Tank truck	
3. Paraformaldehyde	Texas	Hopper cars	
4. Methanol	Texas	Tank cars, some tank trucks	
5. Ammonia	Produced on site		
6. Aromatic solvents	St. Louis	Tank cars	
7. Clay	Southeast	Rail	

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. NH_4Cl		0.19	Discharged to river
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			Burned for fuel
3.			

Disposition of Technical and Formulated Products

Warehouse		Shipments				
		Technical Product		Formulated Products		
On Site	Elsewhere	Container	Transportation	Formulation	Container	Transportation
Most	For distribution (company-owned, controlled)	5%		50-60%, E.C. (10% A.I.)	5-Gal. cans (lined)	Truck > rail
				35-45% Granules	5-lb bags	Truck > rail

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture X Yes ___ No

Pollution control: Process water is discharged to the Mississippi River after mechanical treatment only. Alachlor losses are about 300 lb/day. They are considering the recovery of by-product NH_4Cl. The process has no solid products and gives no off gases. Production equipment requires cleanup only two or three times per year and "presents no problem." The formulation equipment is used for some other products. Packaging area has automatic bagging and filling equipment and is said to be very clean. The production and warehouse areas are not diked. Leaking containers have not been a serious problem: << 1% on bags; < 0.5% on cans. Used drums are a very small problem at Muscaline and would go to a landfill on site. Wipe cloths, etc., are probably burned.

Quality control: Quality control is maintained by G.C. analysis of products before they are packaged. Rework of off-specification batches is no particular problem. Shelf-life is at least 2 or 4 years.

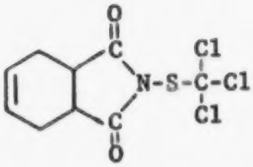
Safety and personnel: "Much emphasis is placed on housekeeping and personnel safety." Work clothes are not provided. Selection of public warehouses for product storage based on having automatic sprinkler system.

General: Monsanto markets through distributors such as co-ops, etc., and alachlor may be available on as many as 15,000 shelves. A small percentage of the production is exported.

CASE STUDY NO. 18

Pesticide: Captan

Chemical name and formula:


O
C
N-S-C-Cl
Cl
Cl
C
O

N-trichloromethylthio-4-cyclohexene 1,2-dicarboximide

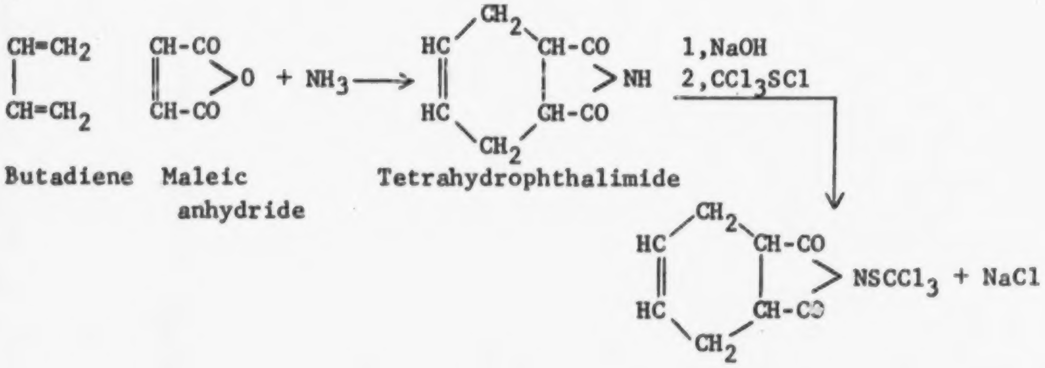
Chemical class: Chlorinated organo-sulfur compound

Pesticide class: Fungicide

Description: Solid; nearly insoluble in water; very low toxicity; non-persistent

Producers: Calhio Chemical (a Stauffer-Chevron subsidiary, Perry, Ohio)

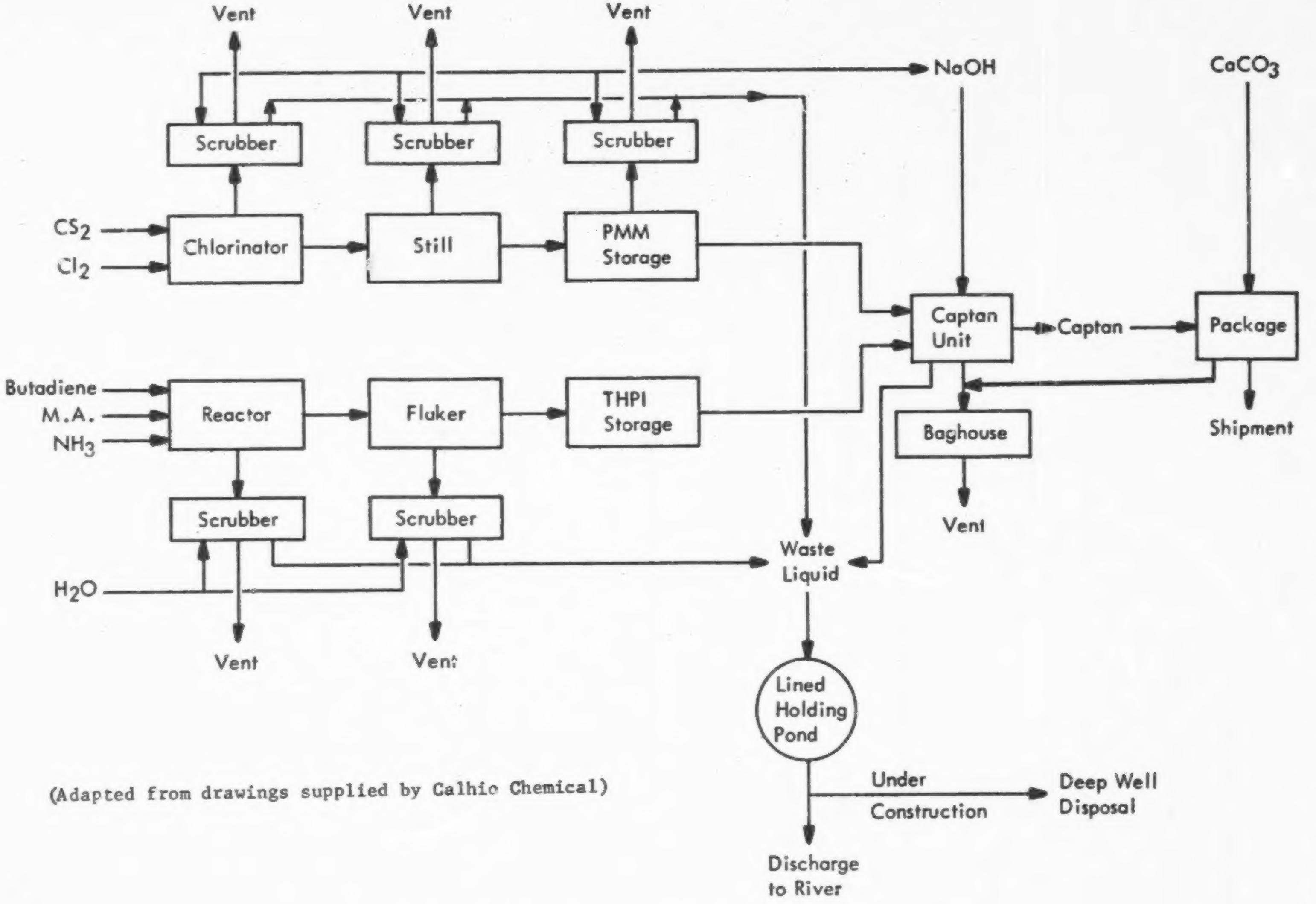
Production chemistry:


CH=CH2
CH=CH2
CH-CO
CH-CO
O
+ NH3
Butadiene
Maleic anhydride
CH2
HC
HC
CH-CO
CH-CO
NH
CH2
Tetrahydrophthalimide
1,NaOH
2,CCl3SCl
CH2
HC
HC
CH-CO
CH-CO
NSCCl3 + NaCl
CH2

Captan

$$CS_2 + 3Cl_2 \xrightarrow{I_2} CCl_3SCl + SCl_2$$

Perchloromethyl mercaptan


Vent
Vent
Vent
NaOH
$CaCO_3$
Scrubber
Scrubber
Scrubber
CS_2
Cl_2
Chlorinator
Still
PMM Storage
Captan Unit
Captan
Package
Butadiene
M.A.
NH_3
Reactor
Flaker
THPI Storage
Baghouse
Shipment
Scrubber
Scrubber
H_2O
Vent
Vent
Vent
Waste Liquid
Lined Holding Pond
Under Construction
Deep Well Disposal
Discharge to River

(Adapted from drawings supplied by Calhio Chemical)

Figure 35 - Production and Waste Schematic for Captan

Production Equipment

Process continuity:

Est. annual production: 18 MM lb/year

Equipment dedication: Also used for Folpet

Plant capacity:

Equipment Age: 1954

Formulation on-site: No

Raw Materials

	Material	Received From	Received By	Storage
1.	CS_2	Delaware	Tank cars	
2.	I_2	Michigan	Drums	Drums
3.	Cl_2	Louisiana	Tank cars	Used directly from tanks
4.	NH_3	West Virginia, Kentucky	Tank cars	Used directly from tanks
5.	$CaCO_3$		Truck loads	Bulk
6.	Maleic anhydride	Missouri, Pennsylvania, New Jersey	Tank cars	
7.	Butadiene	Texas	Tank cars	
8.	NaOH		Tank cars	

Reaction By-Products

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.				
2.				

Other Process Wastes and Losses

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.	Active ingredient	Patriculates	~ 4 lb/day	
2.	Solvents			
3.	Liquid		10 tons/year	Asphalt lined settling pond; discharge
4.	Solid paper		10 tons/year	Local collector
5.	Metal		25 tons/year	Local scrap dealers
6.	Chemical		1,200 lb/year	Buried on plant property

Disposition of Technical and Formulated Products

Warehouse	Shipments				
	Technical Product		Formulated Products		
On-site	Container	Transportation	Formulation	Container	Transportation
3-day capacity only for bags (some outdoor bulk bins)	50-lb bags (92% A.I. 8% $CaCO_3$) (55/pallet)	~ 98% in boxcars 2% in trucks		See text	

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture __X__ Yes ______ No

Pollution control: All liquid effluents from the production facility (including 70-80 gpm dilute saline from the captan unit and that from the scrubbers) go to an asphalt-lined settling pond; retention time is about 6 or 7 days. The effluent from the holding pond (averaging 75 to 80 gpm) goes to a river that feeds into Lake Erie. This effluent is monitored weekly. Captan levels in the discharge are said to be nil. This system has been in operation since the 1950's and no sludge has been removed to date. Depth ranges from 3-1/2 to 4-1/2 ft. Sanitary waste goes to a septic tank.

Calhio is currently testing a new deep well (6,000 ft deep) to be used for liquid wastes. Over 1 million gallons of clean water are being pumped down the well before waste injection can be initiated. This will be the only well in this part of the state; five or six wells are located in the western part of Ohio. Surface facilities for the well have not been designed yet, pending results from the current tests. The well should be in operation by next summer. Capital investment at this plant for environmental protection, including the new deep well, is between $1-2 million,

Solid waste disposal includes: Solid chemical waste--1,200 lb/year (from spills, contaminated waste from floors, etc.) which are buried on plant property; trash paper--cardboard--(10 tons/year), moved out by local collector; metal scrap--(25 tons/year), sold to local scrap dealers.

Air pollution controls include:

Baghouse stacks - 8,000 cfm
Particulates - captan
3.43 lb/day (0.048 grains/ft^3

Filter hood exhaust - 6,500 cfm
Steam
Particulates (captan and water--quantities unknown--less than above)

Packer baghouse stack - 3,500 cfm
Particulates--quantities unknown--less than above

Product change over is about once per year. Clean up is required of the imide and captan processes only. "All" the material from the clean up of these units is salvaged: dust is returned to the broken bag handling system; lumps are slurried and refiltered; and water from the clean up goes into the waste system.

Quality control: Each 10,000 to 12,000 lb of captan are designated as a batch for quality control purposes. A small sample is taken from each 50-lb bag to make up one composite sample for each batch. A titration method is used for AI analysis. They have no particular problems with off-specification materials as it can be reworked without major difficulty.

Shelf-life of the formulated material is not a problem. The function of the $CaCO_3$ in the technical material is to control the pH for better stability.

Safety: Standard safety equipment is used in the plant. All personnel are issued protective masks. Safety standards appropriate for Cl_2 handling are used.

No fires were known that involved captan.

General: Calhio is a jointly-owned subsidiary of Stauffer Chemical Company and Chevron Chemical Company. The technical captan is not an item of commerce; it is shipped only to Stauffer and Chevron, with the exception of an occasional carload shipment to Canada. Captan is formulated by Chevron and Stauffer at 7-10 locations: usually two in New Jersey, two in the Midwest, three or four on the West Coast, and one in Florida (very small quantity only).

Captan is also produced in France in "their" plant and in Israel (Makhteshim?).

Deciduous fruit is the largest use, although there is some use on citrus and seed treatment.

CASE STUDY NO. 19

Pesticide: Methyl Bromide

Chemical name and formula:

$$CH_3Br$$

Bromomethane

Chemical class: Halocarbon

Pesticide class: Fumigant

Description: Liquified gas (BP 3.6°C); very toxic; probably not persistent in sunlight

Producers: Dow (Midland, Michigan); Michigan Chemical; American Potash; Great Lake Chemical; Vulc

Production chemistry:

$$6\ CH_3OH + 3Br_2 + S \longrightarrow 6CH_3Br + H_2SO_4 + 2H_2O$$

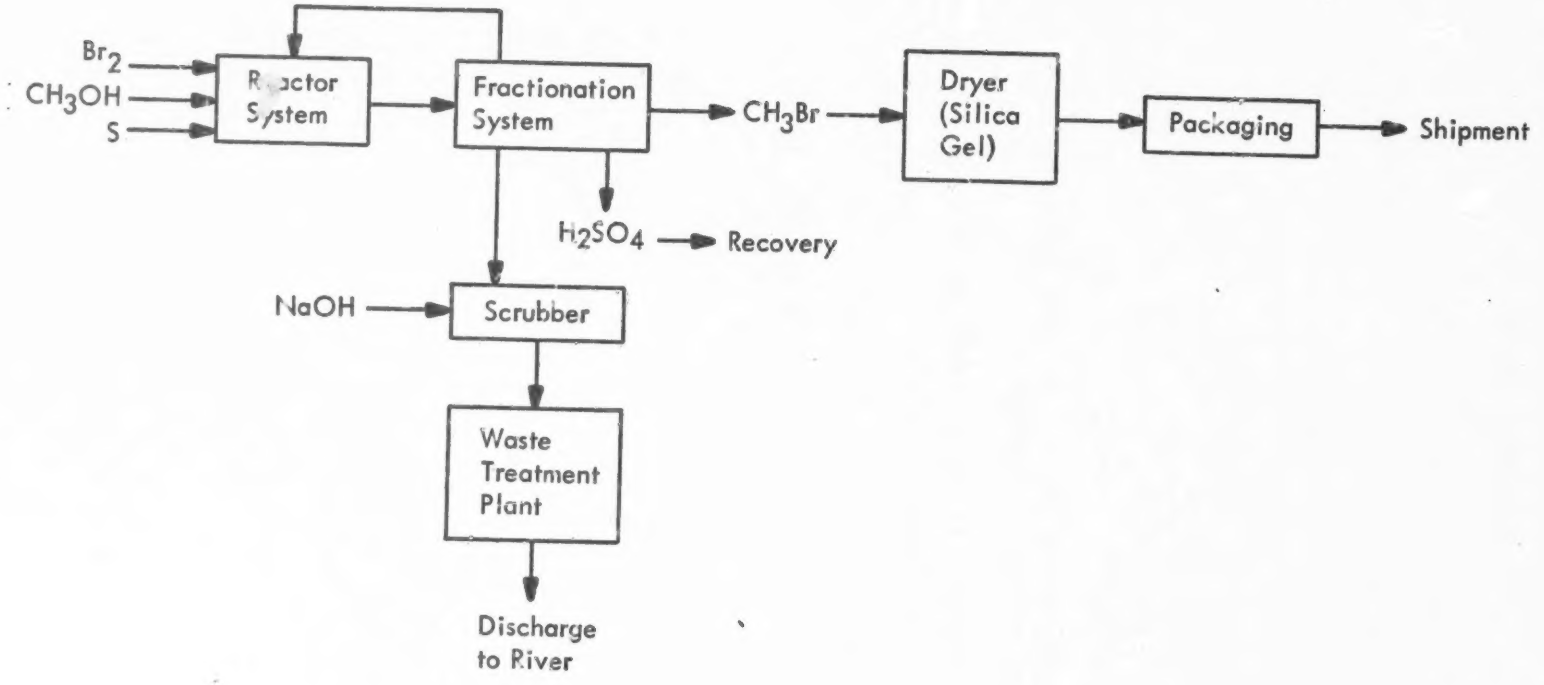

Br_2
CH_3OH
S
Reactor System
Fractionation System
CH_3Br
Dryer (Silica Gel)
Packaging
Shipment
H_2SO_4
Recovery
NaOH
Scrubber
Waste Treatment Plant
Discharge to River

Figure 36 - Production and Waste Schematic for Methyl Bromide (Dow Chemical)

Production Equipment

Process continuity:	Est. annual production: 13 MM lb/year
Equipment dedication:	Plant capacity:
Equipment age:	Formulation on site: Not formulated

Raw Materials

Material	Received From	Received By	Storage
1. Methanol	DuPont	Tank cars or trucks	
2. Bromine	From chlorine production units		
3. Sulfur	Various sources		

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. H_2SO_4		0.183	Recovered
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			
3. Other			

Disposition of Technical and Formulated Products

	Shipments				
Warehouse	Technical Product		Formulated Products		
On-Site	Container	Transportation	Formulation	Container	Transportation
X	1-lb cans				
	10,50,100, 150 lb cylinders				
	1,500 lb pigs				
	13,000 lb cylinders	Export			
	tank cars				

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture _X_ Yes ____ No

Pollution control: Methyl bromide is a colorless, odorless, poisonous gas which requires handling in a closed refrigerated system. By-product H_2SO_4 is recovered; some sold to fertilizer producers; some used to make bromates for photographic purposes. Dow gets $\sim$90% recovery of CH_3Br on first pass (have some recycle streams). A possible by-product is $(CH_3)_2O$ and some of competitors produce considerable. The CH_3Br system is vented through a caustic scrubber and the product is dried with silica gel.

Dow has had almost no accidents with MeBr. Have had almost no leaks on cans or small cylinders; filled cans are checked in a water bath and with halogen leak detector. Dow makes a 9 for 1 offer if a customer gets a leaker. Have recently put in an 18 month shelf-life limitation on cans to guard against corrosion from outside in during storage under poor conditions. Dow uses a shielded type of valve on "pigs" which is drop-proof. Have had minor leaks from sticking valves on tank cars but have handled easily. Biggest problem is the costly reconditioning given to all returned cylinders. Nearly all (90%) of these are Dow-owned and are returnable. Chlorpicrin, a lacrymator, is added to some of the MeBr as a warning agent. See 2,4-D, case study number 13, for further details of Dow's liquid waste disposal system.

Dow produces 50-60% of the CH_3Br in the U. S. with the remainder divided between Great Lakes, Michigan Chemical (St. Louis), Vulcan (Newark), and American Potash (Los Angeles). Some foreign producers also. Probably the largest part of CH_3Br volume goes to commercial applicators, although some goes to packagers (to whom Dow furnishes technical assistance such as on caustic scrubbers). Major shipment areas are:

1. Southeast (North Carolina, etc.) - tobacco, etc. Biggest use probably

2. California - Truck farming

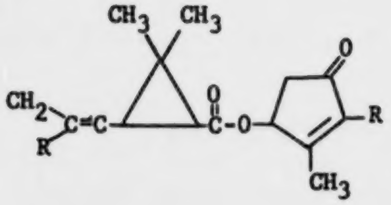
3. Kansas City/Midwest - Grain fumigant

The cost of putting CH_3Br in 1-lb cans is high: (40-50% of price) but Dow fills over 5 million cans per year.

CASE STUDY NO. 20

Pesticide: Pyrethrins

Chemical name and formula:



Several insecticidal components present in the flowers of *Pyrethrum cineraefolium*

Chemical class: Botanical product

Pesticide class: Insecticide

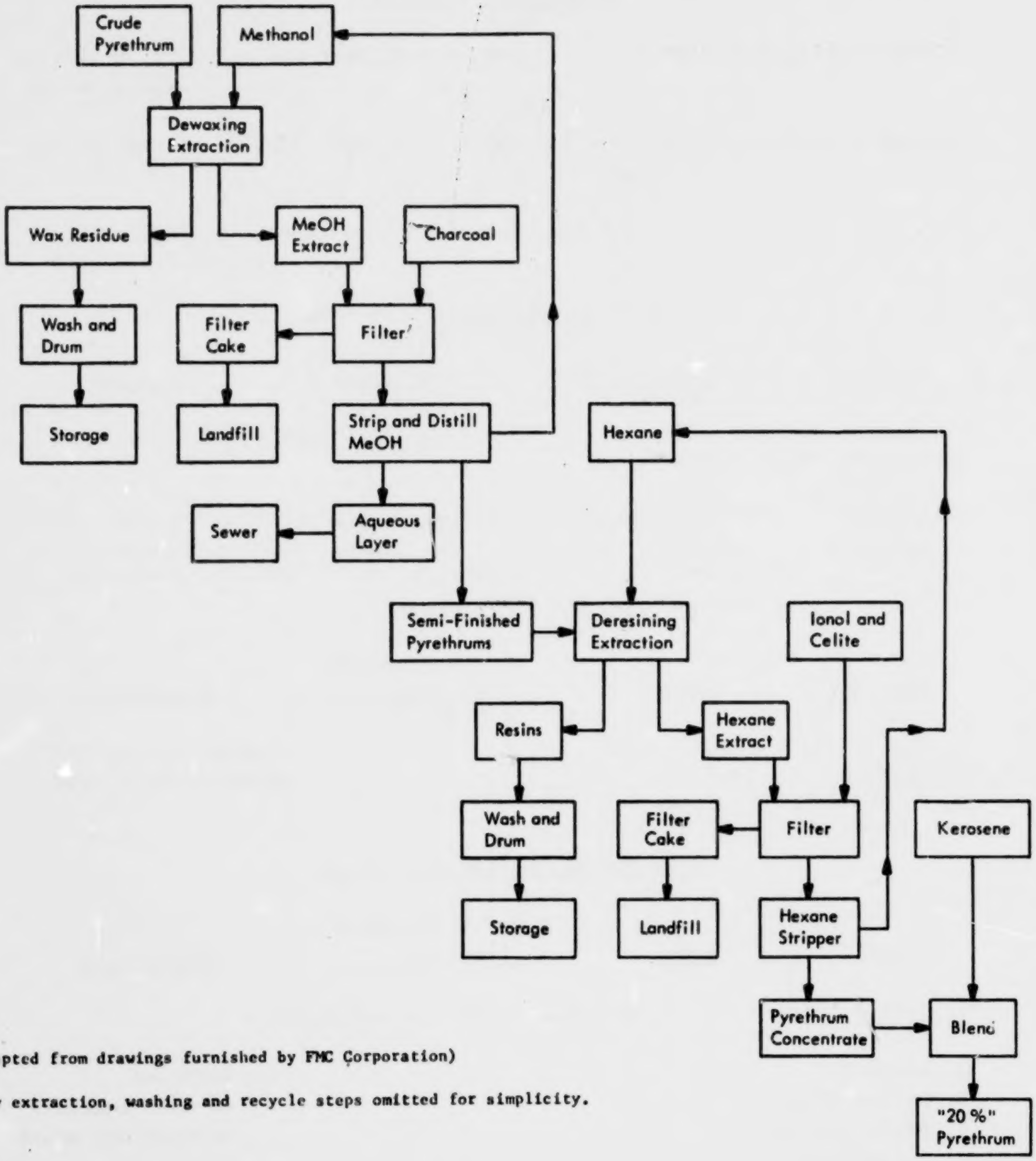
Description: Solid or liquid mixture; low toxicity; nonpersistent

Producers: FMC-Niagara (Baltimore, Maryland and Middleport, New York); McLaughlin Gormley King; Penick

Production chemistry:

Extraction Process

$$\text{Chrysanthemum flowers} \xrightarrow{\text{Solvent}} \text{Crude Extract} \xrightarrow[]{\text{Extract W/}CH_3OH} \xrightarrow{\text{Extract W/}C_6H_{14}} \text{Pyrethrum concentrate}$$


Crude Pyrethrum
Methanol
Dewaxing Extraction
Wax Residue
MeOH Extract
Charcoal
Wash and Drum
Filter Cake
Filter
Storage
Landfill
Strip and Distill MeOH
Hexane
Sewer
Aqueous Layer
Semi-Finished Pyrethrums
Deresining Extraction
Ionol and Celite
Resins
Hexane Extract
Wash and Drum
Filter Cake
Filter
Kerosene
Storage
Landfill
Hexane Stripper
Pyrethrum Concentrate
Blend
"20 %" Pyrethrum

(Adapted from drawings furnished by FMC Corporation)

Many extraction, washing and recycle steps omitted for simplicity.

Figure 37 - Pyrethrum Refinery and Waste Schematic (FMC Corp.)

Producer: FMC Corporation

Production Equipment

Process continuity: Batch

Est. annual production: 130,000 lb/year (100% basis)

Equipment dedication: Pyrethrins only

Plant capacity: 150,000 lb/year (est.)

Equipment age: Est. 30 years avg.

Formulation on site: At Middleport, New York site

Raw Materials

Material	Received From	Received By	Storage
1. Crude pyrethrin	Africa	Drum air freight	Drums
2. Kerosene (deodorized)	New Jersey	Tank trucks	Tanks
3. Lexane	New Jersey	Tank trucks	Tanks
4. Methanol	New Jersey	Tank trucks	Tanks

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Wax	Solid		Drummed and stored
2. Resin	Solid		Drummed and stored
3.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient	Virtually none--too expensive		
2. Solvents			Recycled
3. Filter cakes			On site landfill
4. Resin and wax residues			Drummed and stored
5. Atmospheric losses		Very small	Vent

Disposition of Technical and Formulated Products

	Shipments				
Warehouse	Technical Product[a]		Formulated Products		
On-Site	Container	Transportation	Formulation	Container	Transportation
Available but do not use	~ 100%; 30-gal. drums	Truck to Middleport	Small amt. 12% concentrate	55-gal. drums	Direct to customer
			Rest at Middleport, New York		

---

[a] "20%" concentrate.

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture __X__ Yes ___No

Pollution control: The emphasis on control is to avoid any losses of the active ingredient because of its high price ($52.50/lb, 100%). Extensive recycling is done to minimize losses. Leaks from pump packing, etc. are absorbed on filter aid and recycled. Floor drains in the production area are normally closed to prevent washdown of any spills, and all process drains in the production area are connected to a separation pit. This pit also provided a holding capacity in the event of a large spill. The filter cake is washed, the washings are recycled, and the spent filter material is disposed in an on-site landfill. The bottoms from the MeOH distillation go to a holding drum where the organic layer is separated and recycled. The water fraction is discharged to the sewers and eventually to one of three outfalls. The COD of this water is about 2,000 ppm. The water stream will go into the city sewer system in 1973.

Resin and wax residues from the refining process are currently being drummed and stored: this material will be sold if a market can be developed. Empty crude extract drums are used to store the resin and wax residue. Any excess drums are rinsed with solvent (with washings used in formulation) and then sold to a drum reconditioner. There is some loss of solvents to the atmosphere, but this is thought to be quite small.

The pyrethrin is shipped out of the Baltimore plant in 200 lb net 30-gal. lined drums at a "20%" (21-24%) concentration in deodorized kerosene. Mixing with the synergist, piperonyl butoxide is not done at the Baltimore plant; pyrethrin is shipped to Middleport separately from other toxic materials.

Formulation: Two separate, parallel formulation lines are operated at Middleport: one for residual pesticides and one for non-residual (pyrethrin) pesticides. AI storage is also isolated. The "toxic" formulation area is kept under negative pressure to prevent possible contamination of the pyrethrin area. Floor drains are plugged to avoid any loss of pyrethrin and all of the drums coming into the formulation plant are reused for formulated product.

Most of formulated products go directly to the buyer, but some are warehoused briefly in 11 different locations. Buyers are usually intermediate handlers and formulators or packagers, e.g., aerosol.

Quality control: AOAC methods are used for official purposes, although methods (LGC) are used for internal control. Many physical properties are also seen on the products. Although there are no critical impurities, Fe contamination is a concern. Off-specification material can be reworked with no major problems. No shelf-life problems. Cleanup of equipment is limited to a once a year shutdown for maintenance. The production equipment is used exclusively for pyrethrin production.

General information: The pyrethrin used by FMC is imported as crude extract from the Kenya Marketing Board. One domestic producer, however, does import and sell some flowers.

Generally increased use of pyrethrins is expected. About 40% of current production goes for aerosol use but Niagara does not package aerosols or have retail sales; the remainder goes for a multitude of uses. Pyrethrins, the most expensive pesticide, has been registered in combination with almost all other pesticides. Animal husbandry applications (horse rub) is becoming a significant market.

Producer: McLaughlin Gormley King

Production Equipment

Process continuity:

Est. annual production: 110,000 lb/year (100% basis)

Equipment dedication:

Plant capacity:

Equipment age: Est 30 years avg.

Formulation on site:

Raw Materials

Material	Received From	Received By	Storage
1. Kerosene (deodorized)		Rail (tanks)	Enclosed tank yard or underground tanks
2. All other			
3.			

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.			
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			Recycled
3. Liquid wastes from surface washdown			Municipal sewer system
4. Solid wastes			Contract hauler (to state-controlled disposal)
5. Atmospheric losses		Nil	Vent

Disposition of Technical and Formulated Products

Warehouse On-Site	Shipments				
	Technical Product		Formulated Products		
	Container	Transportation	Formulation	Container	Transportation
X	Steel drums	Truck		Steel drums	Truck

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ____Yes _X_ No

CASE STUDY NO. 21

Pesticide: Bacillus thuringiensis

Chemical name and formula:

$\sim$3% Viable spores of B.t. in organic media

Chemical class: Microbiological product

Pesticide class: Selective insecticide, lepidoptera

Description: Dust; nontoxic to mammals; nonpersistent

Producers: Abbott (North Chicago, Illinois); Nutrilite (Lake View, California)

Production chemistry:

Fermentation Process

$$\text{Nutrient Mixture} \xrightarrow{\text{Sterilize}} \xrightarrow{\text{Innoculate}} \xrightarrow{\text{Ferment}} \xrightarrow{\text{Separate}} \xrightarrow{\text{Dry}} \text{Solid Containing} \sim 3\% \text{ B.t.}$$

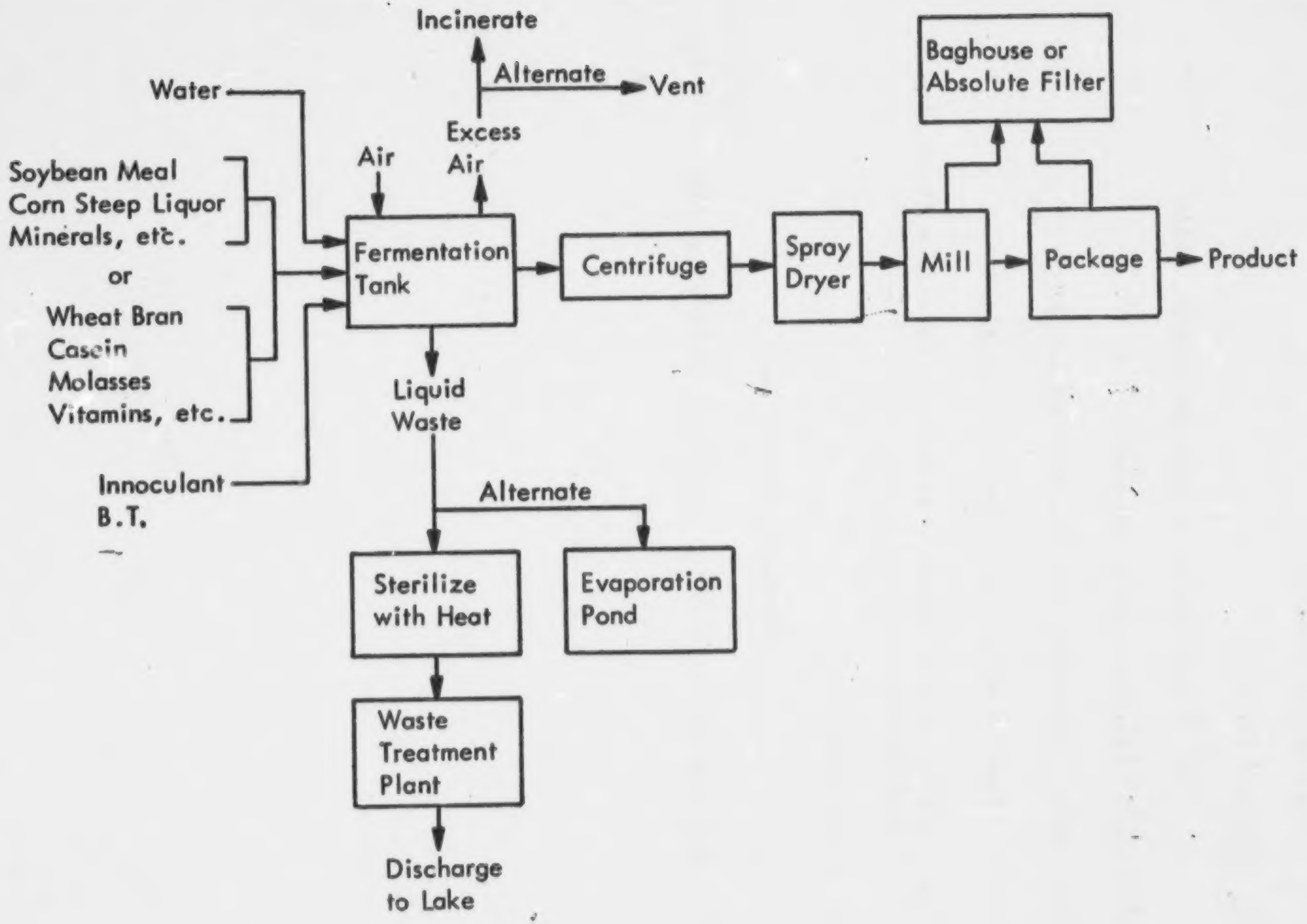

Water
Soybean Meal
Corn Steep Liquor
Minerals, etc.
or
Wheat Bran
Casein
Molasses
Vitamins, etc.
Innoculant
B.T.
Air
Incinerate
Alternate
Vent
Excess
Air
Fermentation
Tank
Centrifuge
Spray
Dryer
Mill
Package
Product
Baghouse or
Absolute Filter
Liquid
Waste
Alternate
Sterilize
with Heat
Evaporation
Pond
Waste
Treatment
Plant
Discharge
to Lake

Figure 38 - Production and Waste Schematic for Bacillus thuringiensis

Producer: Abbott Laboratories

Production Equipment

Process continuity: Batch	Est. annual production: 0.9 million lb/year
Equipment dedication:	Plant capacity:
Equipment age: > 3 years	Formulation on site:

Raw Materials

Material	Received From	Received By	Storage
1. Soybean meal		Rail	
2. Corn steep liquor			
3. Mineral (NaCl etc.)			

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Liquid waste from centrifuge			
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			
3. Other Liquid wastes	Aqueous		Heat sterilized, then to biological waste treatment plant and discharge.

Disposition of Technical and Formulated Products

Warehouse		Shipments				
		Technical Product		Formulated Products		
On Site	Elsewhere	Container	Transportation	Formulation	Container	Transportation
Very little	Mostly in publicly owned warehouses	25-lb fiber drums 2-lb paper bags (12/carton)	Trucks (full loads)	None		

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture__X_Yes ____No

Production: Fermentation process uses nutrient mixture; soy bean meal (received by rail), corn steep liquor, minerals (NaCl, etc) and about 75% H_2O in tanks of 10,000-35,000 gal. The liquid mix is sterilized and the sterile liquid is then innoculated (5 gal/10,000 gal). The fermentation is "submersed" and proceeds aerobically (air is bubbled through) for 2-3 days during which temperature, pH, light and stirring are regulated. Monitor turbidity by visual observation through portholes. The product, a white milky suspension is drained from the tank and centrifuged. The *B.t.* spray dried and the powder is milled and packaged.

Abbott ships in truck load quantities. Use five publicly owned warehouses at present but will use ~20 Abbott-owned ones. Some *B.t.* is reshipped from warehouse by truck to distributors. Some distributors reformulate to dusts, etc.

Pollution control: Raw materials received by rail are unloaded in shed equipped with dust collection equipment. Materials are loaded into fermentation tanks through portholes--no dust problems. Excess air during fermentation goes to an incinerator. Wastewater from the centrifuge is heat sterilized (not required, but good ethical drug practice and good waste control) to kill residual *B.t.* and then sent to the state approved waste treatment plant which treats all Abbott wastes and discharges into Lake Michigan. The centrifuge and spray dryer are contained so that no *B.t.* escapes into the air. The milling and packaging area is enclosed and maintained under "negative" pressure via vacuum take-off through absolute filter:

collected dust is recycled. Filled bags are sealed and vacuum cleaned before coming out of enclosure. Abbott maintains petri dish cultures throughout the plant to monitor for airborne biological effluent.

Quality control: A contaminated fermentation batch would soon show up, be sterilized and disposed--no salvage. No reject batches have been made.

The product contains about 3.2% *B.t.* It is given spore count and biological activity assay (min. is 16,000 internat. units/mg) and also checked for impurities, given mouse test, etc.

The *B.t.* as produced is a unit containing a protein crystal and a spore, both of which contribute to efficacy. Shelf-life is no problem; have stored samples 3 years at 120°F.

General: Abbott sells to distributors such as Niagara and have perhaps 500 outlets. Abbott may also sell directly to very large growers such as Campbells, Birdseye, Libby, etc. Major markets are: in truck-gardening areas in Illinois-Wisconsin; New Jersey; California; and Florida.

Have registration on a number of cole crops (cabbage, lettuce, etc.) and will soon add melons, grapes, ornamental trees, tobacco, etc. Application rate is 0.5-1.0 lb/acre, and most *B.t.* is applied by commercial applicators.

The *B.t.* is found widely in nature and no tolerance is required on presently registered crops. It is nontoxic to mammals, but is toxic to most Lepidoptera larvae, apparently because the high pH (approximately 9) in their gut activates the infection.

Abbott has had no personnel health probelms from *B.t.* production. Studies of possible *B.t.* mutations are underway, but no indication of trouble. Ultraviolet light destroys *B.t.*--keeps it to low level in nature.

Producer: Nutrilite

Production Equipment

Process continuity:		Est. annual production:	0.5 MM lb/year
Equipment dedication:		Plant capacity:	
Equipment age:		Formulation on site:	

Raw Materials

Material	Received From	Received By	Storage
1. Wheat bran	Midwest	Rail	
2. Casein	Locally and New Zealand, Argentina	Tank trucks	
3. Sugar	West Coast	Tank truck	
4. Vitamins		Drums	

Reaction By-Products

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.			
2.			

Other Process Wastes and Losses

Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1. Active ingredient			
2. Solvents			
3. Other: liquid wastes			Evaporative Pond

Disposition of Technical and Formulated Products

	Shipments				
Warehouse	Technical Product		Formulated Products		
On-Site	Container	Transportation	Formulation	Container	Transportation
	25-lb lined fiber-board containers	Truck			

Pollution Control Regulation

1899 Refuse Disposal Act applies to this manufacture ___Yes _X_No

Production: Nutrilite produces B.t. as a wettable powder in 5,000-lb batches. All of the product is shipped to a single formulator/distributor, Thompson-Hayward who apparently formulates in Los Angleles, Fresno, New Orleans. Dusts: 1.5% and 2.5% on clay and bait 3% on corn meal.

Pollution control: Wastewater is nontoxic and is sent to settling pond where it evaporates. The grinding operation is controlled by cyclone/baghouse. No odor problems during manufacture.

Quality control: Raw materials are food grade. They analyze for heavy metals (emission spectroscopy) and insecticides such as DDT and PCB's (G.C.) as these are deadly to growth. Cannot really monitor a batch as it is growing, as spore count takes 4 days and bioassay 2 weeks, but do use turbidity as a check. Each batch has to be tested for safety (mouse test, Botulinus, etc.)--no failures--and for effectiveness. Shelf-life is good unless temperature gets high; ex. 200°F for 2 weeks--may keep for 5 years at 125°F. Must make sure that spores are not exposed to water which generates bacterium.

CASE STUDY NO. 22

Pesticide: Mercury compounds

Chemical name and formula:

Mercury Chlorides

(Mixture of $HgCl_2 + Hg_2Cl_2$)

Chemical class: Heavy metal

Pesticide class: Fungicide

Description: Solids; variable water solubility; most are very toxic; persistent

Producers:

Production Chemistry:

$$Hg + Cl_2 \longrightarrow Hg_2Cl_2$$

Mercurous chloride

$$Hg + HNO_3 \longrightarrow Hg(NO_3)_2 \xrightarrow{H_2SO_4} HgSO_4 \xrightarrow{NaCl} HgCl_2$$

Mercuric chloride

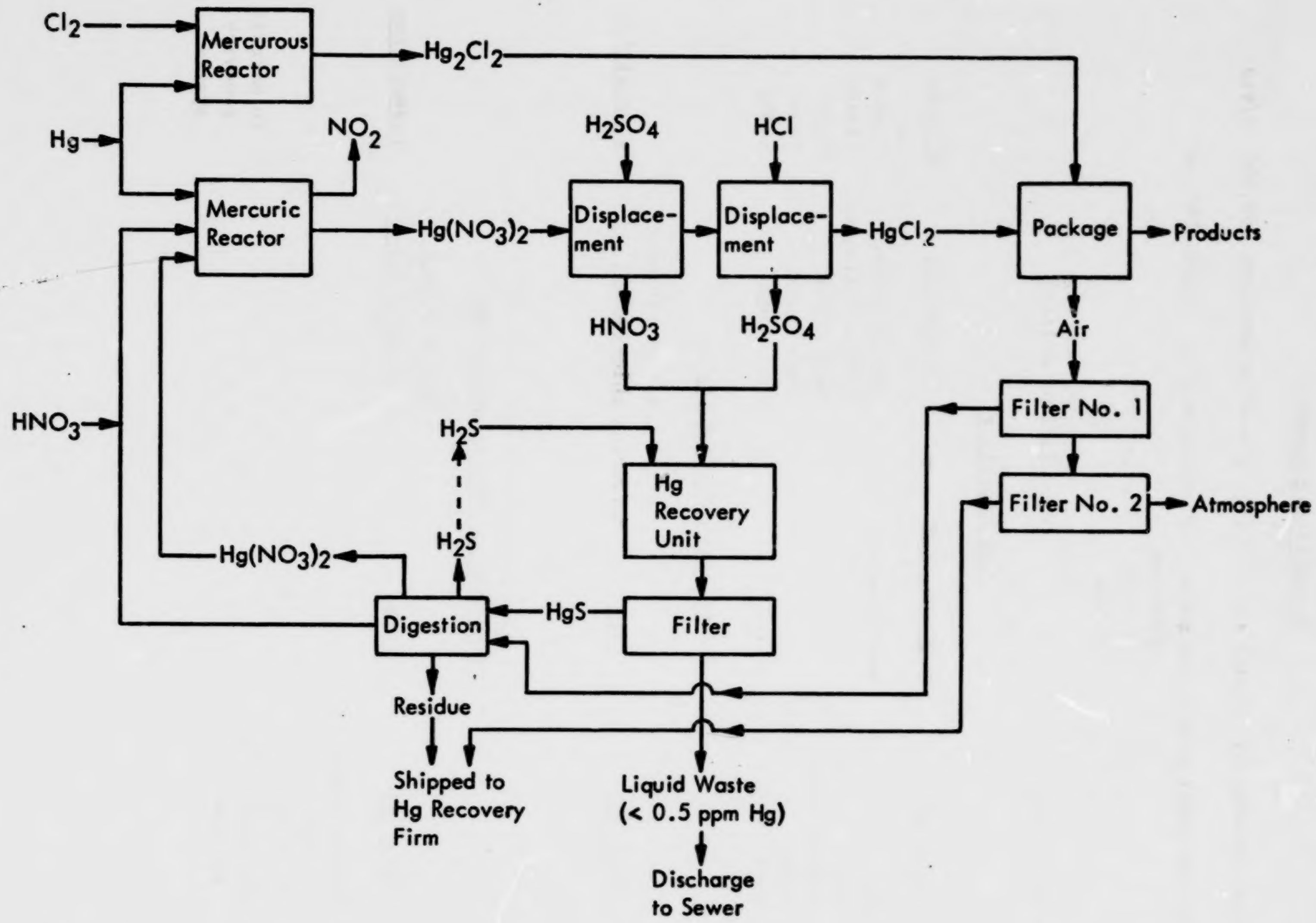

Cl_2
Hg
HNO_3
Mercurous Reactor
Mercuric Reactor
NO_2
Hg_2Cl_2
$Hg(NO_3)_2$
H_2SO_4
HCl
Displace-ment
Displace-ment
HNO_3
H_2SO_4
$HgCl_2$
Package
Products
Air
Filter No. 1
Filter No. 2
Atmosphere
H_2S
H_2S
Hg Recovery Unit
Filter
HgS
$Hg(NO_3)_2$
Digestion
Residue
Shipped to Hg Recovery Firm
Liquid Waste (< 0.5 ppm Hg)
Discharge to Sewer

Figure 39 - Production and Waste Schematic for Mercury Chloride

Production Equipment

Process continuity: Batch

Est. annual production: 50,000 lb/year

Equipment dedication: Separate equipment for each process

Plant capacity: 50,000 lb/year

Equipment age:

Formulation on-site:

Raw Materials

	Material	Received From	Received By	Storage
1.	Hg°	Most overseas	76-lb flasks	Flasks
2.	Cl_2		250-lb cylinders	Flasks
3.	HNO_3		Tank truck	Tanks
4.	H_2SO_4		Tank truck	Tanks
5.	NaCl		Tank truck	Tanks

Reaction By-Products

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.				
2.				

Other Process Wastes and Losses

	Material	Form	Amount Produced (lb/lb A.I.)	Disposition
1.	Active ingredient			
2.	Solvents			
3.	All wash water and waste			To mercury recovery system

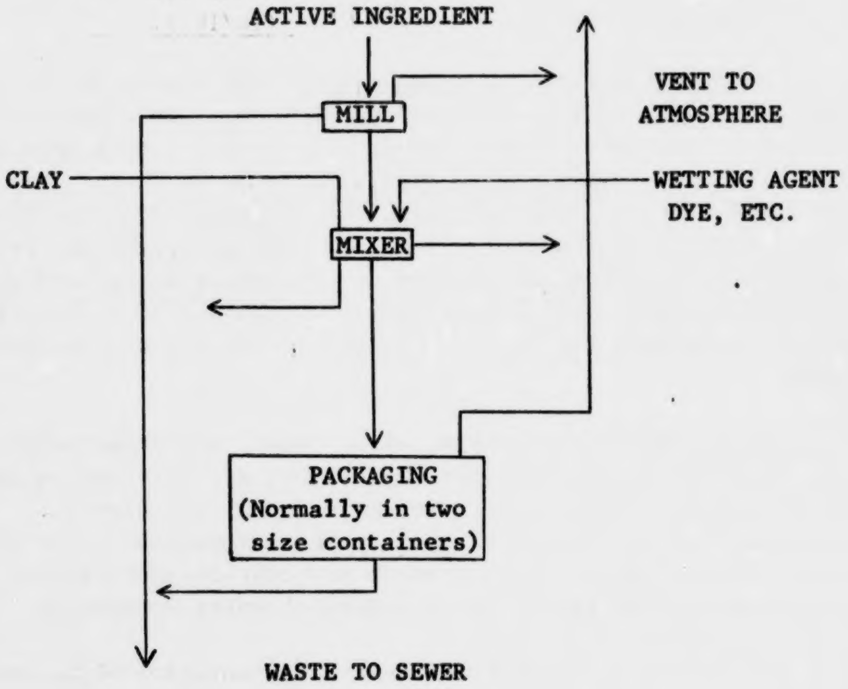
Disposition of Technical and Formulated Products

Warehouse		Shipments				
		Technical Product		Formulated Products		
On-Site	Else-Where	Container	Transportation	Formulation	Container	Transportation
St. Louis	If needed Jersey City and Los Angeles	10-gal. fiber pak drums	Piggy-back, exclusive use trucks, rail			Piggy-back

Pollution Control Regulation

1899 Refuse Disposal act applies to this manufacture X Yes ______ No

Formulation process: The mercury compounds are shipped to St. Louis for formulation. The formulation process is rather typical. The active ingredient is normally milled by itself before being added to the other ingredients. The process for the mercury chloride formulations is depicted in the following diagram.


ACTIVE INGREDIENT
MILL
VENT TO ATMOSPHERE
CLAY
WETTING AGENT DYE, ETC.
MIXER
PACKAGING (Normally in two size containers)
WASTE TO SEWER

All five mercury formulations are made in the same equipment.

Pollution control in manufacture: All wash water and wastes from the active ingredient manufacturing plant go to a mercury recovery system where it is precipitated with H_2S. The mother liquor from this recovery contains about 100 to 500 ppb of Hg, and is discharged to the sewer (part of the New Jersey Sewer Authority). Concentration of mercury in the actual outfall is <100 ppb. This effluent contains only a small quantity of mercury. All residue from the acid redigestion operation are drummed and shipped to a mercury recovery company in Houston, Texas, although analysis of the residue indicates that it contains no mercury.

The only solids generated from these processes are from the decontamination of process equipment. This material is drummed up with the other waste material sent to Houston for mercury recovery.

The finished material is filled in hooded filling tables. The hoods exhaust to two filter systems. The first filter elements are periodically removed and processed through the acid-digester mercury recovery system. Filter elements from the second system go into the drummed material sent to Houston for mercury recovery.

All work clothes are given a preliminary wash on site before being sent out for final washing. Water from this preliminary wash goes to the mercury recovery system.

They have had no odor complaints.

Pollution control in formulation: The sewers in the plant area are sumped (collected) and all washings are caught in floor trenches leading to the sump. The washings are periodically pumped into a special tank and treated with sodium hydroxide to precipitate the mercury. This material is then filtered into a second tank with the collected liquors being reused for wash down during the product run. Solids collected from the recovery operation are packed in drums and shipped to the active ingredient production plant to recover the available mercury. At the end of a production run or if the volume becomes too great; treated, filter liquors are released to the sewer.

Rags, liners from raw material drums, and other material that might come in contact with active ingredients are returned to the active ingredient production plant for mercury recovery and disposal. Uniform contamination has not been a problem in this operation but in the event it happened, company policy is to prewash any contaminated uniform prior to its being returned to the vendor for standard cleaning procedures.

Effluents from the hoods in the fermentation plant are vented to the atmosphere.

Quality control: Quality control is maintained by Hg analysis and specific impurities: sulfide, sulfate content, other heavy metals. As these are batch processed, rework of off-specification materials is not a major problem.

General: Some of this material is exported, apparently not a major part of the production. Shipments would go out of the new York port. Major shutdowns are unusual. The last one was about 2 years ago, to repair a chlorine burner. About once a week, however, something requires a minor repair.

Safety: Workers are checked by weekly blood and urine analysis.

D. Summary of Pollution Aspects Based on Case Studies

The case studies developed a considerable amount of information on the practices of the pesticide manufacturers which is related to the overall pollution potential. Because of the diversity of processes used for the different pesticides, and the different pollution control practices employed, comparison is difficult; but several aspects are worthy of discussion.

1. Raw materials: The raw materials used for the synthesis of many pesticides are hazardous materials and some pollution potential is inherent in the transportation and handling of materials of this nature. Some of these materials are flammable, some are corrosive and poisonous, and some may be exceptionally toxic to fish if spilled into waters. However, the transportation of these materials are subject to close governmental regulation and the handling practices of the pesticide manufacturers are as good as or better than those of industry in general.

The raw material which is common to the most pesticides is elemental chlorine which is used directly on-site in the production of chlordane, toxaphene, 2,4-D, 2,4,5-T, atrazine, captan, carbaryl and mercuric chloride and is used to prepare raw materials brought in for the production of DDT, Aldrin-Dieldrin and perhaps also trifluralin and alachlor. The production of this chlorine formerly involved extensive use of the mercury cells which led to the well-publicized mercury losses. Now, however, these cells are being better controlled and are being gradually displaced by the mercury-free diaphragm cells. Dow Chemical's Midland facility, which uses the diaphragm cell and Chipman appear to be the only facilities among those studied here which use on-site chlorine generation. Most of the producers of the other products mentioned receive Cl_2 in tank car quantities by rail with the exception of Geigy's new St. Gabriel plant which receives Cl_2 by pipeline.

Other materials of unusually hazardous nature which are transported by rail, barge or truck include hydrogen cyanide (of which over 10 million pounds are required for atrazine), carbon disulfide, various amines, and the concentrated acids and caustic. The P_2S_5 used in all the organophosphorus pesticides, the C_5Cl_6 used for aldrin, and numerous other materials also pose some hazard. Time did not permit an in-depth study of actual vs. potential pollution caused by the transport of all these materials, but overall the record appears to be relatively good.

The raw materials may be stored on-site in bulk storage facilities, but in many cases are drawn directly from the shipping container (e.g., tank car or tote bin) and used in the production processes. The handling of materials such as chlorine are apparently in conformity with good industrial practice codes such as those of the Chlorine Institute. Instances of accidental spills of raw materials were mentioned which required special cleanup and disposal procedures, e.g., a phenol spill by a tank truck operator during transfer to company storage facilities. In many cases scrubbers or dust collection equipment are used in the raw material unloading areas.

2. Production processes: The manufacturing processes for pesticides vary considerably from product to product, but two characteristics are generally present which may differentiate the pesticide industry from many if not all of the large industries which are of environmental pollution concern: (a) the ingredients handled or produced have unusually high toxicity to some animals (e.g., man or fish) or plant-life; and the production processes normally require only low or moderate temperatures, compared, for example, to industries producing ore- or rock-derived products. Because of the toxicity of the materials handled, production facilities were designed to include a great many safety features to minimize occupational hazards. Because of the moderate temperature, air pollution control of good efficiency could be largely adapted from existing technology. Water pollution control, as will be discussed in a subsequent section, poses a much more difficult problem than air pollution in the pesticide industry.

The production plants for the 22 key pesticides studied range from capacities of 1 million pounds per year or less to about 100 million pounds per year and the plant equipment ranges from 1 year old to over 20 years old and in at least two cases the plant buildings are over 50 years old. In general, the more toxic materials such as the organophosphorus and carbamate insecticides and some of the herbicides which have undergone rapid growth recently (such as atrazine) are produced in newer plants, while many of the older chlorinated hydrocarbons and other products are produced in somewhat older equipment. However, almost none of the plants have been designed since the advent of the recent increased consciousness of environmental concern, and most of the companies interviewed have recently completed, are building, or are designing new pollution control equipment to bring their plants into conformity with local standards.

The production equipment is used in almost every case either for only one product or for two very similar products, i.e., two products of the same chemical family and with similar pesticidal applications. Cleanup of equipment is therefore minimized and is small compared to that required in a formulation plant where many products are processed through the same equipment. In cases where solvent cleanup of process equipment is required, the used solvent is generally reused as a matter of economics by recycle to the process, or it may be used in formulation, or combusted for fuel purposes.

Most of the companies interviewed have farily extensive contingency plans. Many of them maintain a company fire department and others state that they work closely with local fire departments, but this cooperation could probably be improved in nearly all cases.

Good practice dictates that production facilities be diked and that runoff from malfunction, spills, fire extinguishment, etc., can be contained in a holding pond or pit until treated, so that over-loading of the conventional waste treatment plant is avoided. In many, but not all plants, this procedure is in effect and in some cases is said to serve as a safety for recovery of valuable product.

All the manufacturers of the 22-key pesticides have on-site quality control laboratory facilities and frequently monitor the raw materials and reaction intermediates as well as the final product. In almost no case, it would seem, is a production run of such poor quality or so far "off-specification" that it cannot be used--either blended off with a higher quality batch or reworked to remove objectionable impurities.

The efficiency of the synthesis reactions as commercially conducted is generally regarded or proprietary information. Similarly, the efficiencies of recovery of products, by-products and unreacted starting materials are not available. Unfortunately, even data on the quantities of these materials being discharged or disposed by those manufacturers who must file under the Refuse Disposal Act of 1899 became available during this study on only a few plants. These data indicate, however, that discharges of active ingredients range from undectable or but a few pounds per day to nearly 1,000 lb/day. (At the lower levels the difference becomes a problem of analytical sensitivity, of course, since a level of only 1 ppm in the discharge from a large plant may mean several pounds per day.) The efficiency of recovery in the past has often depended on the price of the product balanced against the difficulty of recovery, and hence, a widely and easily produced material like DDT was discharged in sizable quantities. The present trend is toward better recovery and water economy in order to minimize treatment or disposal costs.

3. Storage, handling and shipping: The use of most pesticidal products is seasonal with the major application occurring during the spring or summer season. Therefore, production and formulation also tend to be seasonal in order to avoid building up undesirably large inventories. Among the manufacturers of the key pesticides studied, several noted that their production peaked in late winter or early spring; and some stated that they did not produce during the summer months. On the other hand, most companies do produce the year around and also may formulate on site so that extensive storage facilities are required. A brief summary of the formulation and warehousing practices of the producers of key pesticides is given in Table XV. Production site storage in bulk or tank car quantities is sometimes practiced, but long-term storage appears to be more often in drums.

TABLE XV

SUMMARY OF FORMULATION AND WAREHOUSING ACTIVITIES BY KEY PESTICIDE PRODUCERS

Company	Product	Formulation at Production Site[a]	Product (Technical or Formulated) Warehoused On-Site[b]
Montrose	DDT	Some	Yes
Shell	Aldrin	~10%	Some
	Dieldrin	No	Some
Velsicol	Chlordane	No[c]	Small, tank car amounts
Hercules	Toxaphene	Only a dust concentrate	Yes[d]
Chemagro	Disulfonton	Yes	Drum only
American Cyanamid	Malathion	~1%	No
	Phorate	No[c]	Yes
Monsanto	Parathions	< 5%	Yes
Union Carbide	Carbaryl	No[c]	Some
	Aldicarb	No[e]	No
Dow	2,4-D	Yes	Yes
Chipman	2,4-D	Yes	Some
Dow	2,4,5-T	Yes	Yes
Thompson-Hayward	2,4,5-T	Yes	Yes
Geigy	Atrazine	Yes	No
Lilly	Trifluralin	Yes	No[d]
Monsanto	Alachlor	Yes	Yes
Calhio	Captan	No[e]	Very little
Dow	Methyl Bromide	No	Yes
FMC	Pyrethrins	No[e]	Negligible
Abbott	*Bacillus t.*	No	No
Nutrilite	*Bacillus t.*	No	No
Mallinckrodt	$HgCl_2$-Hg_2Cl_2	No[e]	Yes

---

[a] Formulation is by customer where not otherwise indicated.

[b] Warehoused by customer or in public warehouse where not otherwise indicated.

[c] Portion formulated at contractor facilities.

[d] Company warehouses or bulk storage at other locations.

[e] Formulation at company facilities at another location.

Good storage practices dictate that different pesticides be stored separately, or at least in well-marked locations within a warehouse. In cases where a company handles more than one pesticide at a given location, special care is usually taken to keep herbicides well segregated from fungicides and insecticides, but pesticides which are similar chemically and in activity may be produced in the same equipment and stored in the same area.

The storage facilities of the major producers appear to be generally well regulated to prevent accidental losses of pesticides during handling and storage and well equipped with fire protection. These facilities, however, are not as frequently diked as are the production areas. Similarly, most companies appear to specify such fire protection equipment as automatic sprinklers when they use public warehouses, but few of these are diked. Thus, warehouse fires which require use of large amounts of water are a serious potential source of pesticide pollution. The further the warehouse is from the control of the primary producer, the greater the potential in an estimated majority of cases.

The mode of transportation of pesticides away from the production sites to the customer, distant storage facility or formulator varies widely because of the variations in location of production sites and use areas. The products are shipped by various combinations of rail and truck, depending on the nature of the material, packaging practices and the marketing structure. Shipping containers range in size from gallon cans and small bags to 6,000-gal. tanks. A general outline of the packaging and transportation practices is given in Table XVI. The Department of Transportation regulates transportation of pesticides by rail and motor carrier.

The packaging and transportation practices generate different pollution potentials for different products. Most of the highly toxic organophosphates such as disulfoton and the parathions are never shipped in tanks--only drums. (A part of the less toxic malathion is shipped in tanks.) Similarly, the toxic carbamates are shipped as 50-lb bags, in the case of carbaryl, and in two specially modified tank trucks (which are nearly "roll-proof") in the case of the extremely toxic aldicarb. The shipment of liquid pesticides (and particularly toxic organophosphates) in drums reduces the potential for a large spill of hazardous material, but the handling and disposal of the emptied drums are a serious problem. On the other hand, most of the toxaphene is shipped in tank cars and trucks and transferred directly into company-owned bulk storage tanks at the formulators' location and no used drums are generated in this step.

TABLE XVI

SUMMARY OF PACKAGING AND TRANSPORTATION PRACTICES FOR KEY PESTICIDES

Pesticide	Transportation Mode	Packaging
DDT	Boxcars > Trucks	Bags > fiber drums
Aldrin-dieldrin	Truck and rail	Fiber drums
Chlordane	Rail and truck	Drums > tank cars and trucks
Toxaphene	Rail and truck	Tank cars and trucks > drums and bags
Disulfoton	Truck >> rail	Drums
Malathion	Truck and rail > sea train	Drums > tank cars and trucks
Phorate	Truck and rail	Drums
Parathions	Truck >> rail	Drums
Carbaryl	Rail > piggyback or truck	Bags
Aldicarb	Truck	Special tank truck
2,4-D (Dow)	Rail (and trucks?)	Tank cars = bags and drums
2,4-D (Chipman)	Rail and truck	Tank cars and trucks, drums, cans
2,4,5-T	Rail and truck	Mostly drums
Atrazine	Rail	Bags > plastic cans
Trifluralin	Rail and truck	Cans
Alachlor	Truck > rail	Cans and bags
Captan	Rail	Bags
Methyl bromide	Rail and truck?	Cans and cylinders (10-13,000 lb)
Pyrethrin	Rail or truck	Drums
Bacillus t.	Trucks	Drums and bags
$HgCl_2$-Hg_2Cl_2	Piggyback truck/rail	Drums

A significant difference in pollution potential exists between transport in tank cars and tank trucks. Tank cars are either company-owned or leased by the company from the railroad, and are used over and over for the same or a similar product. If the tank car requires cleaning between shipments or before return to the railroad (as during the slack season), cleanup is done at the production site and wastes go to the company's detoxification or disposal system. Tank trucks on the other hand normally are received from the trucking firm in a clean and dry condition, are filled, then transported to the destination and unloaded by the trucker, who then has the responsibility for cleanup before the truck goes to another customer. The trucking firm, however, normally does not have the detoxification and decontamination equipment nor the technical expertise available at the manufacturer: washings are probably most often disposed in the most convenient manner.

Pesticides which are packaged in cans, drums and bags are very often shipped from the manufacturers only in truckload or carload lots. In many cases, however, as the distribution system fans out, consignment becomes less than carload or truckload lots and the pesticides become part of mixed lot shipments. In such cases the manufacturer loses some control over the product and it may be shipped together with flammable solvents or other material which might increase the pollution potential.

In summary, the storage handling and shipping practices of the manufacturer are generally well regulated and supervised, but accidents can occur.

4. By-products and wastes: Virtually every pesticide production process produces aqueous or gaseous streams and frequently solid wastes which contain unreacted ingredients, unrecovered products and solvents, and unavoidable or undesired by-products. Extensive efforts are usually made to minimize by-products and to recover, recycle, or otherwise prevent these process losses from occurring. For each process, however, a balance point is eventually reached between the expense of recovery and the value of the recovered product. In the past, the economic considerations were frequently dominant and process losses were included as unavoidable costs. Under the recent emphasis on environmental contamination further efforts have been made to recover many previously lost materials--even when economics indicated that it was more expensive to do so--and most pesticide manufacturers have invested in or are in the process of building extensive waste treatment facilities wherein those wastes which cannot be recovered are degraded to acceptable levels or disposed by state approved methods. A summary of the principal waste generated and the disposal method employed by the producers of the key pesticides is shown in Table XVII.

While most of the companies interviewed indicated that they are presently in conformity with local standards, a quantitative picture of the overall pollution potential could not be developed during this program. Under the 1899 Refuse Act Permit program, those companies which discharge to navigable waters have been filing discharge data with the Corps of Engineers, but unfortunately, these data started to become available only very late in our study (Part B of the applications was due in October). These data indicated that in several instances, sizable amounts of unreacted raw materials or unrecovered active ingredients are discharged (see Appendix C), but these materials are generally not the persistent pesticides.

TABLE XVII

SUMMARY OF MANUFACTURING WASTES AND DISPOSAL

	Liquid Wastes		Solid or Other Wastes	
Pesticide	**Source**	**Disposal**	**Source**	**Disposal**
DDT	Processing solutions	Evaporative basin	Reactor solutions	County Dump
Aldrin	Floor washings, etc.	Evaporation basin	Lime slurry	Lime pit
Dieldrin	Process solutions	Evaporation basin	Filter solids	Incinerate
Chlordane	Process solutions	Deep well	Filter solids	Clay pit
Toxaphene	Pinene-Camphene plant	Bio-treatment plant		
	Process solutions	Neutralize, hold, discharge	Filter solids	Solid waste
Disulfonton	Process solutions	Secondary treatment plant	Filter solids, etc.	Commercial landfill
			H_2S	Flare
Malathion	Process solutions	Barge to deep sea	Filter solids	Landfill (with lye)
Phorate	Process solutions	Barge to deep sea	Filter solids	Landfill
			Mercaptan losses	Flare
Parathions	Process solutions	Waste treatment plant	H_2S; S	Flare; incinerate
Carbaryl	Process solutions	Secondary waste treatment	H_2, $COCl_2$, amine	Flare
			Heavy residues	Incinerate
Aldicarb	Process solutions	Neutralize, secondary waste treatment	Process vents	Flare
2,4-D (Dow)	Process solutions	Trickling filter; biological waste treatment plant	Filter solids and still bottoms	Incinerate, Scrub
2,4-D (Chipman)	Process solutions	Charcoal absorption/ filtration treatment	-	-
2,4,5-T (Dow)	As per 2,4-D			
2,4,5-T (Thompson-Hayward)	Process solutions	Oxidation pond, discharge	Solids	Landfill
Atrazine	Process solutions	Most to river; some to deep well		
Trifluralin	Process solutions	Biological waste treatment	NO_x	Scrubber
Alachlor	Process solutions	Discharge	Solvent	Fuel
Captan	Process solutions	Hold, discharge	Gas streams	Scrub, vent
Methyl Bromide			Gaseous wastes	Scrub, waste treatment plant
Pyrethrin	Aqueous still bottoms	Sewer	Process solids	Storage
Bacillus t. (Abbott)	Process solutions	Sterilized; biological waste treatment	Filter solids	Landfill
Bacillus t. (Nutrilite)	Process solutions	Evaporation pond	Process air	Incinerate or filter
$HgCl_2$-Hg_2Cl_2	Process solution	Hg-recovery; discharge to sewer	Filter solids	Hg recovery
			NO_x, H_2S	Recovery

The producers of the persistent chlorinated hydrocarbons use: an evaporative basin, in part* for DDT; an evaporative basin for dieldrin; and deep well disposal for chlordane. Therefore, these plants have no discharges subject to the 1899 Act. The evaporative basins require a word of further comment: evaporative and wind blown losses from these facilities require evaluation and the long-term future of the basin should be considered, e.g., what happens if the production site is closed 25 years from now and converted to other (even residential) uses?

Deep well disposal is also used by several pesticide producers in states where that practice is permitted. Sea disposal is also practiced by a number of producers in the eastern seaboard area and one report states that 329,000 tons of pesticide wastes were disposed at sea in 1968,[5/] but the amount of active ingredients of any kind were not specified.

The air pollution aspects of pesticide production are essentially without quantitative data. The only air pollution data which we have seen on pesticides are for ambient air samples: i.e., almost no emissions data on specific pesticides from a given plant have been published. These data are much needed.

A number of minor sources of pesticide losses were noted during the interviews. One of which has received the attention of a few companies is the small amounts which collect on workers clothing, wipe cloths, etc. Good data on losses on shoes, etc., are simply unavailable, although one company noted that they had reduced miscellaneous losses from 150 to 2 lb/day by increased vigilance to small details. Some companies furnish all production workers with clothing which is then collected and washed or prewashed in a company run laundry from which the wastewater goes to detoxification treatment. On the other hand, some pesticide producers utilize commercial laundries which may wash the company's materials separately from all others, but do not use any special detoxification treatment. The use of disposable clothing and cloths also requires attention to see that these materials are incinerated rather than go to a landfill if the contaminant is a persistent pesticide.

Another potential pollution source is contaminated solvents which might be sent to a solvent reclamation service. None of the major manufacturers appear to do this, but smaller producers or formulators may (particularly with solvents used for cleanup purposes). The pesticide content of the solvents may be concentrated in still bottoms or on filter media which are not detoxified.

---

* DDT - containing liquids do go to an approved county Class 1 dump.

5. Cleanup and decontamination of equipment: Equipment cleanup is an integral part of pesticide manufacture. This operation is both time consuming and expensive, and therefore, is kept to an absolute minimum. Equipment cleanup is generally required for one of two reasons: (1) for equipment maintenance, or (2) for quality control purposes.

Repair and preventive maintenance of production equipment is a continuing process. This is due not only to the types of equipment used, but also to the age of the production facility (new to over 20 years old).[6] Corporate philosophy on maintenance varies from scheduled shutdowns of the complete production unit to only unscheduled shutdowns of specific items of equipment for needed repair. Generally, continuous processes require a scheduled shutdown whereas batch operation can be maintained on a less rigid schedule. In either case, the equipment must be emptied of toxic material before it can be opened for inspection or repair.

Quality control necessitates the cleanup of production equipment when the same facility is used for production of different active ingredients. This is frequently the case when two or more pesticides can be manufactured by the same process. Parathion and methyl parathion, for example, are made in the same production unit by using essentially the same process and the appropriate alcohol.[7] Extensive cleanup between different process runs is necessary to prevent possible cross-contamination. Production scheduling that minimizes the number of product changes is used to reduce this type of cleanup as much as possible. Product change-over usually involves cleanup of only that portion of the process that would contain potential contaminants. Conversion from the production of Captan to Folpet, as an example, requires the cleanup of only one of the three unit processes involved.[8]

Cleanout procedures generally involve flushing the production system with a solvent. In some cases, steam also is used.[9] Wastes from these cleaning operations normally go into the plant's process-waste system.

The pollution potential associated with equipment decontamination and cleanup is not particularly significant. First of all, only a small quantity of active material is involved in this operation, much less than 1% of the equipment capacity. Of more importance is the fact that wastes generated by equipment cleanup in almost all cases go into the plant waste systems. Thus, the pollution that could result from discharge of these wastes is primarily dependent on the efficiency of the waste handling system.

6. Safety practices: Safety practices in the pesticide production industry are designed for both the protection of the workers and the containment of highly toxic or dangerous chemicals. The degree and sophistication to which safety measures are used are primarily dependent on the hazard involved.

Three types of pesticides require special environmental control: (a) the organophosphates, because of their anticholinesterase activity; (b) the chlorinated hydrocarbons, because of their stability; and (c) the carbamates which also have anticholinesterase activity. Effects from these, as well as other toxic pesticides, may be produced by swallowing breathing, or absorption through the skin.[10/] Personnel protection measures and devices are designed to prevent these three types of contamination.

Coveralls, boots, gloves, goggles, and a variety of respiratory devices are used to protect production workers. In addition, exhaust ventilation systems are used where there is a potential for atmospheric vapor, spray, or dust containing active ingredients, for a hazardous raw material or intermediate. These devices seem to protect personnel from respiratory and dermal routes of intoxication.

Protection against ingestion of toxics is a matter of personal hygiene which is largely the responsibility of the individual worker. Hands and face should be thoroughly washed before eating, drinking, or smoking. Tobacco, food, beverages, or gum should not be brought into the pesticide production area. These guidelines help prevent poisoning resulting from ingestion.

Figures 40 and 41 illustrate the range of toxicities encountered and the variations in the sophistication of safety practices that might be expected. The facility for manufacturing aldicarb, one of the most toxic pesticides made in the United States, utilizes highly refined precautions, including air suits for maintenance and decontamination, and glove-cabinets at toxic sample points. Respirators are issued to all personnel who come on the plant site. Less toxic pesticides, such as carbaryl, only require the use of standard personnel safety equipment.

The containment practices and equipment used are also commensurate with the hazard involved. Fire, explosion, and toxicity risks are considered. Control devices commonly used for containment include diking the production area, vacuum operation of process vessels, and caustic scrubbing of process vents.

Medical facilities are a part of the overall safety program found at pesticide plants. Both preventive medicine and first aid services are provided. Typical medical services include a periodic physical examination, first aid for minor cuts or burns, and periodic cholinesterase tests for employees potentially exposed to anticholinesterase pesticides (organophosphates and carbamates).

The potential for environmental damage resulting from inadequate safety equipment and procedures apparently exist for some facilities that are not adequately prepared to handle emergency situations. Contingency plans specifically designed to handle fires, explosions, or vandalism involving pesticide production plants are not universally available.

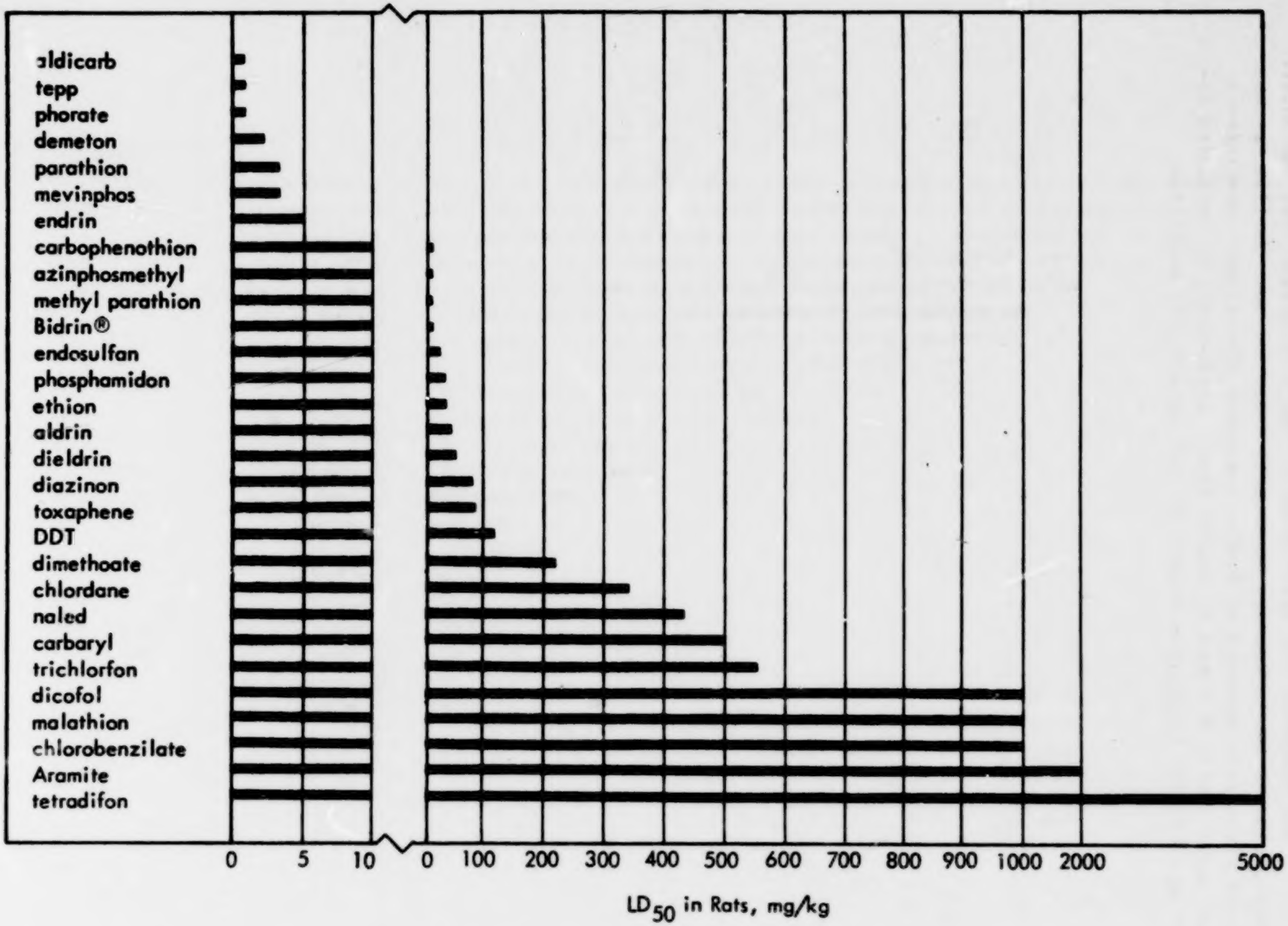


Figure 40 - Acute Oral Toxicity10/

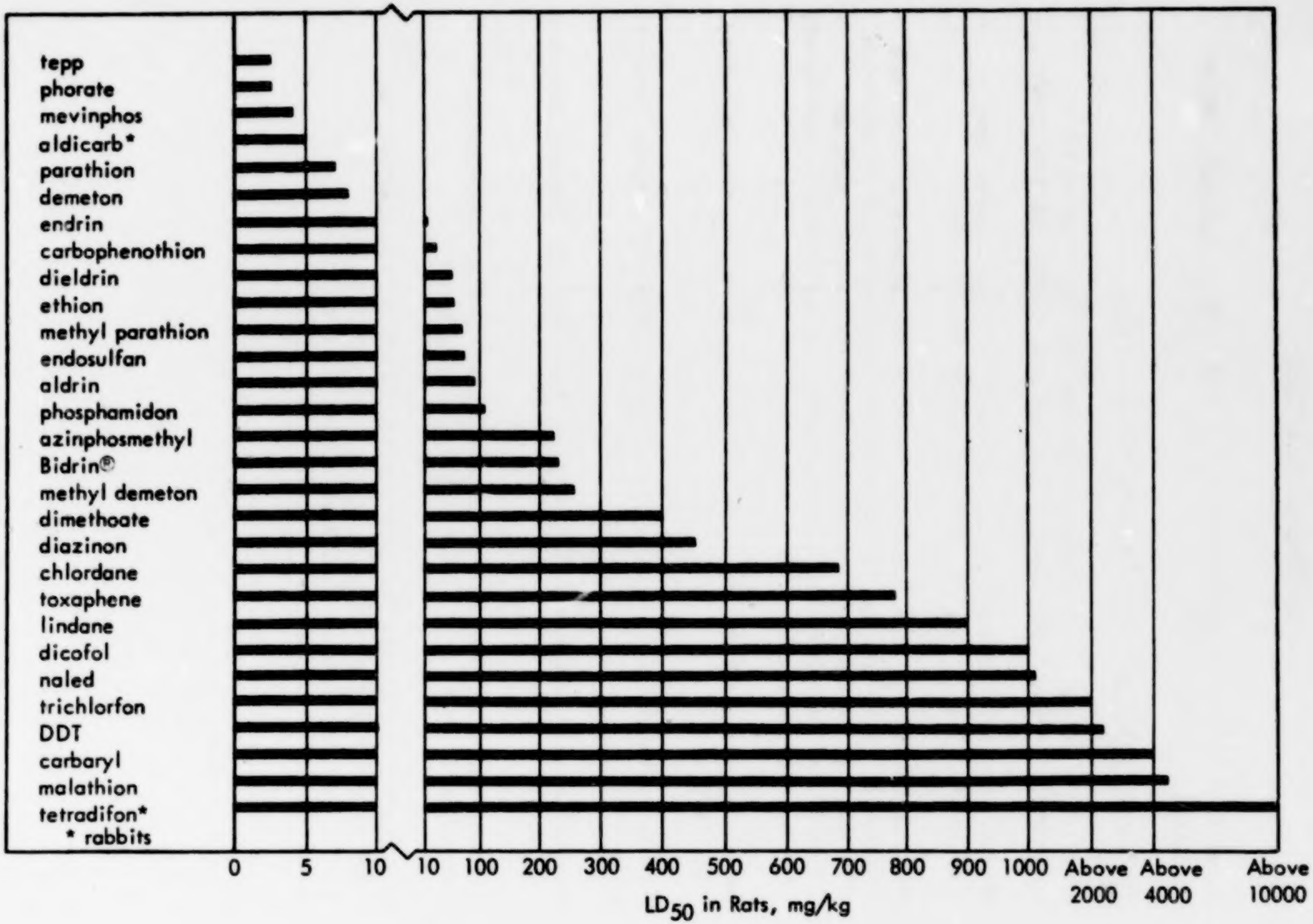


Figure 41 - Acute Dermal Toxicity10/

LITERATURE REFERENCES

1. Schmidt, T. T., R. W. Risebrough and F. Gress, Bull. Environ. Contam. Toxicol., 6, 235 (1971).

2. Air/Water Pollution Report, p. 285, July 12, 1971.

3. Greek, B. F. and F. E. Rosenberger "Design and Construction of a Phosphate Insecticides Plant," Ind. and Eng. Chem., 51, 104 (1959).

4. Henshaw, Tom B., "Absorption/Filteration Plant Cuts Phenols from Effluent," Chem. Eng., 78, (12) pp. 47-49, May 31, 1971.

5. Breidenbach, A. W., "Application of Solid Waste Research to Pesticide Disposal," presented at The National Working Conference on Pesticide Disposal at National Agricultural Library, Beltsville, Maryland, June 30 and July 1, 1970, U. S. Department of Agriculture, Washington, D. C., September 1970.

6. Personal communication, Mr. Jack G. Copeland, Hercules, Inc., November 19, 1970.

7. Personal communication, Mr. Joe W. Gillespie, Monsanto Company, October 11, 1971.

8. Personal communication, Mr. Don Gohlson, Cook Chemical Company, November 9, 1971.

9. Personal communication, Mr. J. H. Bees, Union Carbide Corporation, November 3, 1971.

10. Safe Use of Pesticides, The American Public Health Association, Inc. New York (1967).

V. FORMULATION OF PESTICIDES

The general nature of the art of formulating active chemical compounds into finished, ready-to-use pesticides has been described on pages 33-36. In this section the various aspects and practices of the pesticide formulation industry which relate to potential environmental pollution are discussed. Interviews and plant-site visits were conducted during the course of this study with the formulators, packagers, and distributors listed in Table XVIII, in addition to several manufacturer-formulators already listed in Section IV, in order to gain an understanding of the industry as it exists today.

TABLE XVIII

SUMMARY OF FORMULATORS, PACKAGERS, AND DISTRIBUTORS VISITED

Arlington Blending and Packaging Company	Formulation	Arlington, Tennessee[a]
Chapman Chemical Company	Formulation	Memphis, Tennessee[a]
Chase Chemical	Aerosol Packaging	Chicago, Illinois[a]
Coahoma Chemical Company	Formulation	Clarksdale, Mississippi[a]
Cook Chemical Company	Aerosol Packaging	Baton Rouge, Louisiana[a]
E-Z Flow Chemical	Formulation and Distribution	Lansing, Michigan[a]
FMC-Niagara	Formulation	Fresno, California
Helena Chemical Company	Formulation	West Helena, Arkansas
Michlin Chemical Corporation	Formulation and Distribution	Detroit, Michigan[a]
Pulvair Corporation	Formulation	Memphis, Tennessee[a]
Riverside Industries	Formulation	Marks, Mississippi[a]
Thompson-Hayward	Formulation	Fresno, California
Valley Chemical Company	Formulation	Greenville, Mississippi
Wilbur-Ellis Company	Formulation	Los Angeles, California
Wilbur-Ellis Company	Formulation and Distribution	Fresno, California

---

[a] Office visit only.

A. Formulation Facilities

Although virtually all pesticides are formulated before they are used, formulating is not necessarily done at the site of active ingredient manufacture, or by the active ingredient manufacturer. Thus, formulation facilities must be evaluated in light of both ownership and location patterns.

1. Producer-formulator: The producer-formulator, or integrated producer, not only manufactures the basic active ingredient but also formulates it in his own facilities into a marketable product. Such formulation facilities may be located at the site of active ingredient production or in major use areas. (See Table VII and Figures 5-10.)

Generally, this type of facility is used for the production of only a few formulations. Safety and operating standards are in keeping with the corporate philosophy.

2. Independent formulators: The independent formulation operation involves the processing of active ingredients into formulated pesticides under one of several business arrangements.

One common practice is the contract formulation of proprietary pesticides for the active ingredient manufacturer. In this type of operation, formulation technology, the active ingredient, and operating assistance are provided by the basic manufacturer. The formulated product is marketed under the basic manufacturer's label. Frequently, an independent formulator will have contracts of this type with several active ingredient manufacturers.

Many independent formulators package and sell pesticides under their own label. These operations, however, generally limit their marketing to the use area in which they are located.

Another category of formulation facilities combines these two operations by producing formulated pesticides under their own label as well as proprietary formulations for active ingredient manufacture.

Farm cooperatives are an important class of independent formulators because they handle a significant part of the pesticides used for agricultural purposes. In 1962-1963, for example, farmers purchased about 19% of their pesticides through cooperatives.[1/] A major portion of these pesticides was formulated by the cooperatives in their own formulation facilities.

The independent formulators, as most formulation facilities, are generally located within the use area that they service. As has been shown in the section on geographical locations of producers (page 54), active ingredient producers are frequently located at sites remote from major use areas, and therefore, from many formulators of their active ingredient.

3. Small packagers: There are some packagers in the United States for whom pesticide formulation is a minor part of their operation. These packagers frequently process a wide mixture of materials that include paint, perfume, pesticides, and other specialty items.

This type of operation, however, is the least significant in terms of quantity of pesticide formulated. These formulators generally service a small geographical area in which they are located.

4. Aerosol packagers: Aerosol packaging is a unique segment of the pesticide industry. About 100 million aerosol pesticide containers are packaged per year.[2] It has been estimated that over 90% of these containers are filled by six companies.[3]

The formulation of aerosols is essentially a mixing process. In some cases, the aerosol formulator is supplied with a concentrate containing all ingredients of the aerosol except solvent and propellant. The only operations required in this case are dilution of the concentrate with the appropriate solvent and filling.

Many of the facilities that fill pesticide aerosols also fill other product lines, such as paint, varnishes, disinfectants, air fresheners, and specialty items. The major fillers of pesticide aerosols, however, generally have filling facilities used exclusively for pesticides. The names and locations of the major pesticide aerosol filling plants are shown in Table XIX and Figure 42. Pesticides account for about 8% of the aerosol containers packaged in the United States as shown in Figure 43.[4]

B. Pollution Potential in Pesticide Formulation

The preceding sections on major pesticide formulations (page 33) and types of formulation facilities illustrate the diversity of operations involved in this industry. The pollution potential that results from pesticide formulation can be best evaluated by considering the basic elements required for all formulation activities.

1. Raw materials: Three basic raw materials are required for pesticide formulation: (1) the active ingredient; (2) other chemicals that make up the formulated products (solvents, inert carriers, dyes, etc.); and (3) containers.

The active ingredients are received in containers ranging in size from 5 gal. up to tank cars and tank trucks. Generally, the active ingredient shipping container is used as the storage vessel, and the active ingredient goes directly from the storage container into the formulation process equipment.

TABLE XIX

AEROSOL PESTICIDE FILLING PLANTS

Major Filling Facilities

S. C. Johnson and Son, Inc.	Racine, Wisconsin
Boyle-Midway	Cranford, New Jersey
ATI (Aerosol Techniques, Inc.)	Los Angeles, Danville, Illinois; Milford, Connecticut
Con-Wood Corporation (Hot Shot)	Memphis, Tennessee
Ban-Stalfort	Philadelphia, Pennsylvania
Chase	Chicago, Illinois
ATI (Aerosol Techniques, Inc.)	Boston, Massachusetts
Peterson-Puritan	Danville, Illinois; Rhode Island
Cook Chemical	Baton Rouge, Louisiana
Aerosols, Inc.	Neodesha, Kansas

Other Filling Facilities

Purex Corporation	Lakewood, California
E. A. Thompson	San Francisco, California
Parrott Chemical Company	Stamford, Connecticut
Sprayway	Chicago, Illinois
Tripple-X	Chicago, Illinois
Boyer Chemical Company	Evanston, Illinois
Tripple-X	Mundelein, Illinois
Camie Company	St. Louis, Missouri
Midwest Consultants	St. Louis, Missouri
Orb Industries, Inc.	Media, Pennsylvania
Delta Chemical Corporation	Memphis, Tennessee

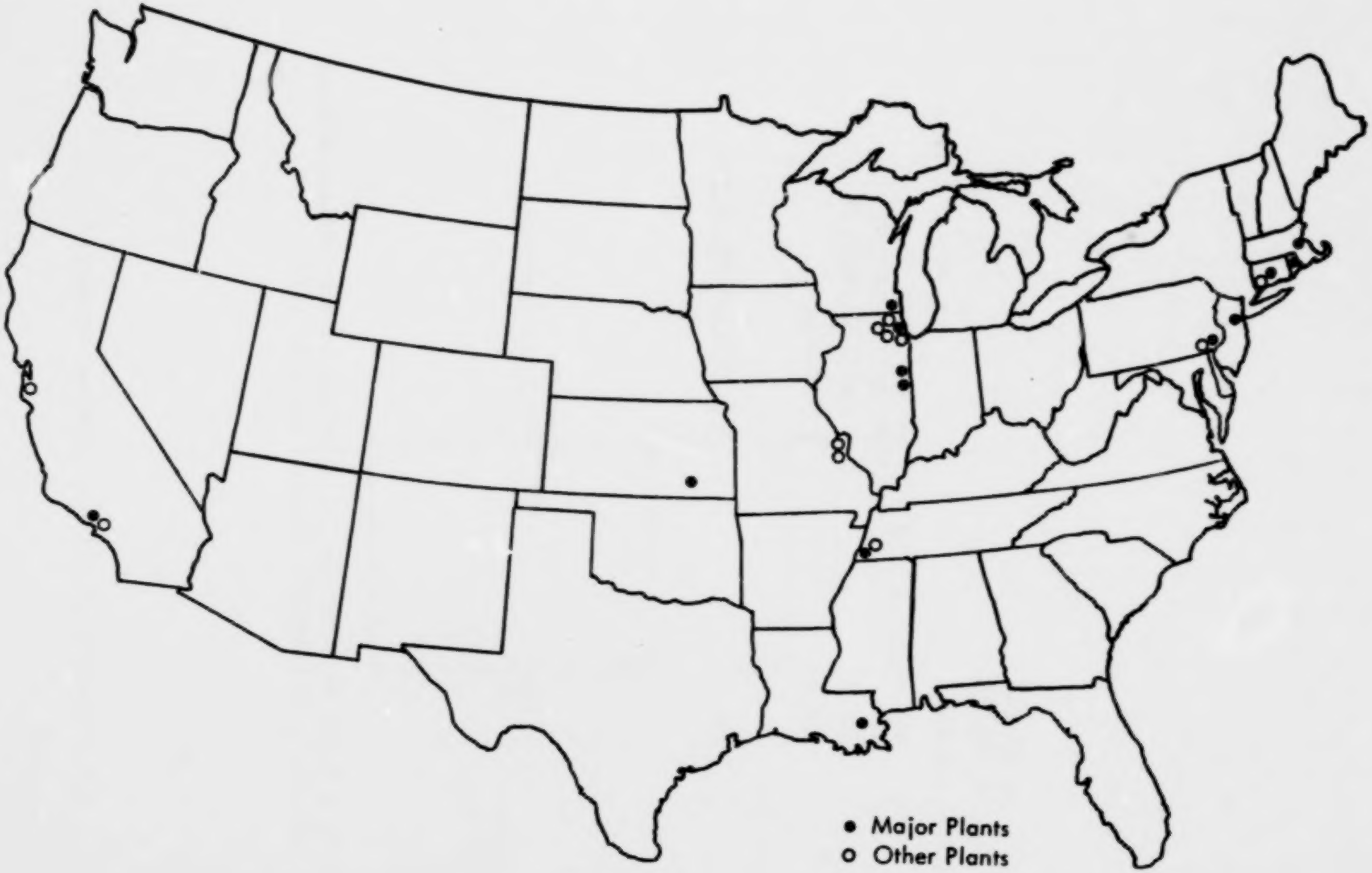
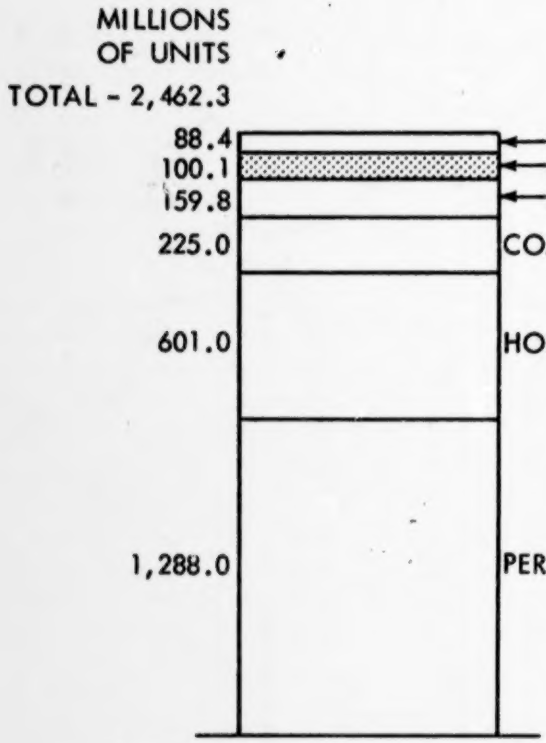

● Major Plants
○ Other Plants

Figure 42 - Pesticide Aerosol Filling Plants



Source: Working Group on Pesticides, Proceedings of the National Working Conference on Pesticide Disposal (July 1, 1970).

Figure 43 - 1969 United States Aerosol Container Production

Other chemicals are received by virtually all available means and in all sizes of containers. Wherever economically feasible, large volume chemicals, such as solvents, are received in bulk. Bulk chemicals are either stored as received, e.g., in tank cars, or they are transferred into bulk storage tanks.

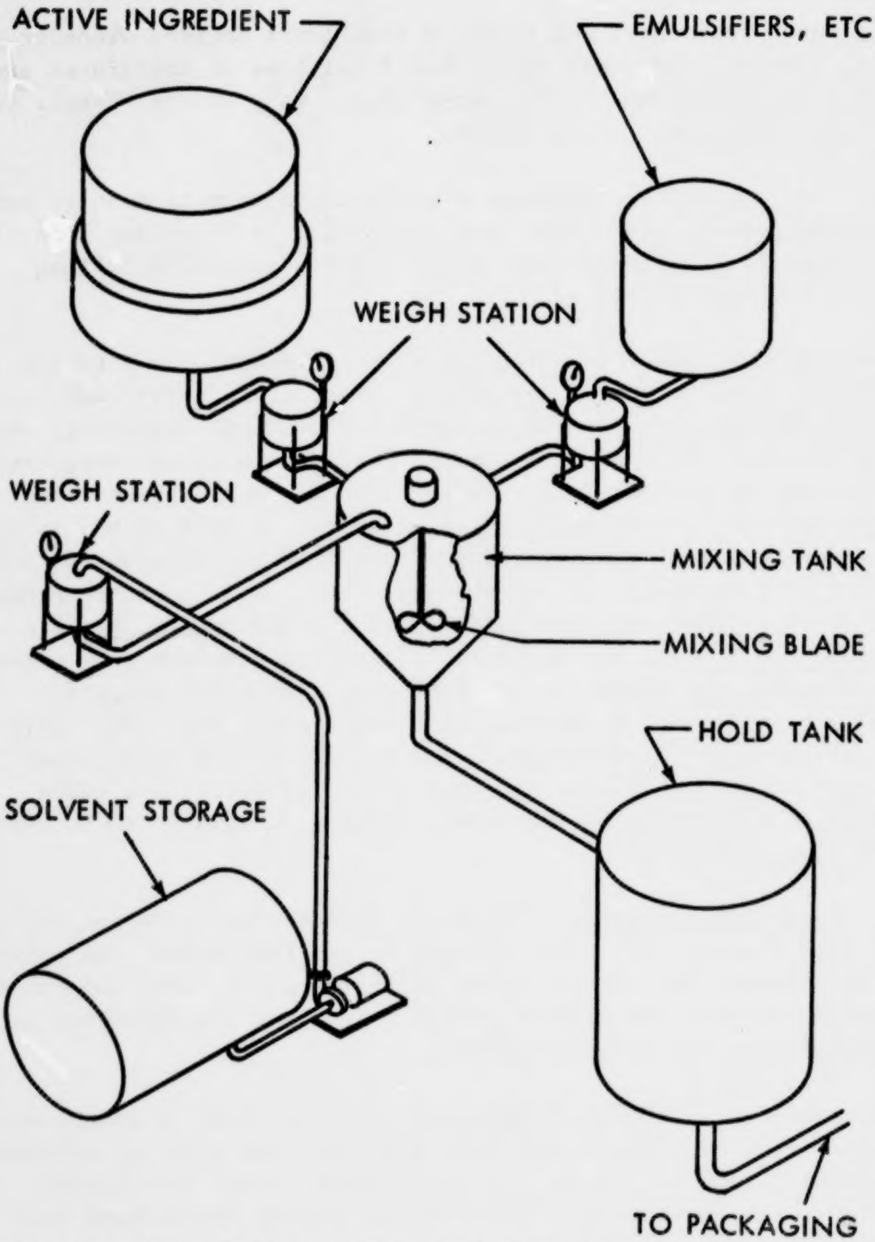
The empty containers are received from local sources whenever possible. Paper, plastic, and small (less than 5 gal.) metal containers are normally stored in a warehouse before being used. Many of the 55-gal. drums, however, are stored outdoors until needed.

Spot or statistical sampling of empty containers is done in most cases. This technique has generally been successful in detecting lots of defective containers. The inspection of all containers before filling, however, is not commonly practiced.

The greatest pollution potential associated with raw materials is the chance of spilling the active ingredient before it is introduced into the formulation process. The active ingredient receiving, unloading, and storage areas observed for nonbulk shipments were generally not adequately diked or otherwise equipped to deal with spills.[5-8] Bulk shipment and storage areas, however, are normally better equipped to deal with a spill. Potential for environmental contamination exists from the cleanout of some bulk containers used for shipping active ingredient. Rail cars are generally in dedicated service (used only for shipment of a given active ingredient), and are periodically cleaned at the active ingredient manufacturing plant. Tank trucks, however, are generally not used exclusively for a specific active ingredient, and must, therefore, be cleaned after each use. This cleaning is the truckers responsibility, and is done at his or at other commercial truck washing stations. In some cases, effluent from these washing facilities is discharged into sewer systems or held in evaporation ponds without being treated.[9]

2. Formulation process: Pesticide formulation processes are primarily batch mixing operations. The desired active ingredient, the appropriate carrier or solvent, and the necessary additives are blended and milled in the ratios needed to give the desired active ingredient concentration and physical properties in the finished product.

An example of a liquid formulation plant is given in Figure 44. The active ingredient is proportioned into a mixing tank with the correct amounts of solvent, such as xylene and emulsifying agent, and blended. Both weight and volume measurements are used to achieve the desired proportions.


ACTIVE INGREDIENT
EMULSIFIERS, ETC.
WEIGH STATION
WEIGH STATION
MIXING TANK
MIXING BLADE
HOLD TANK
SOLVENT STORAGE
TO PACKAGING

Source: Toxaphene Bulletin 621, Synthetics Department,
Hercules, Inc., Wilmington, Delaware

Figure 44 - Liquid Formulation Process

The finished batch is normally stored in either the mixing tank or a hold tank until the material can be analyzed to ensure that it meets specifications.

Dust and powder formulations require mixing and milling operations (see Figure 45). The inert carrier material commonly comes in 50-lb bags. These bags are broken open into a pit which feeds a conveyor to a weigh hopper. This hopper feeds into a mixer or blender where the inert is sprayed with a solution of the active ingredient. This mixture is then milled to achieve the desired pesticide size before being filled into containers.

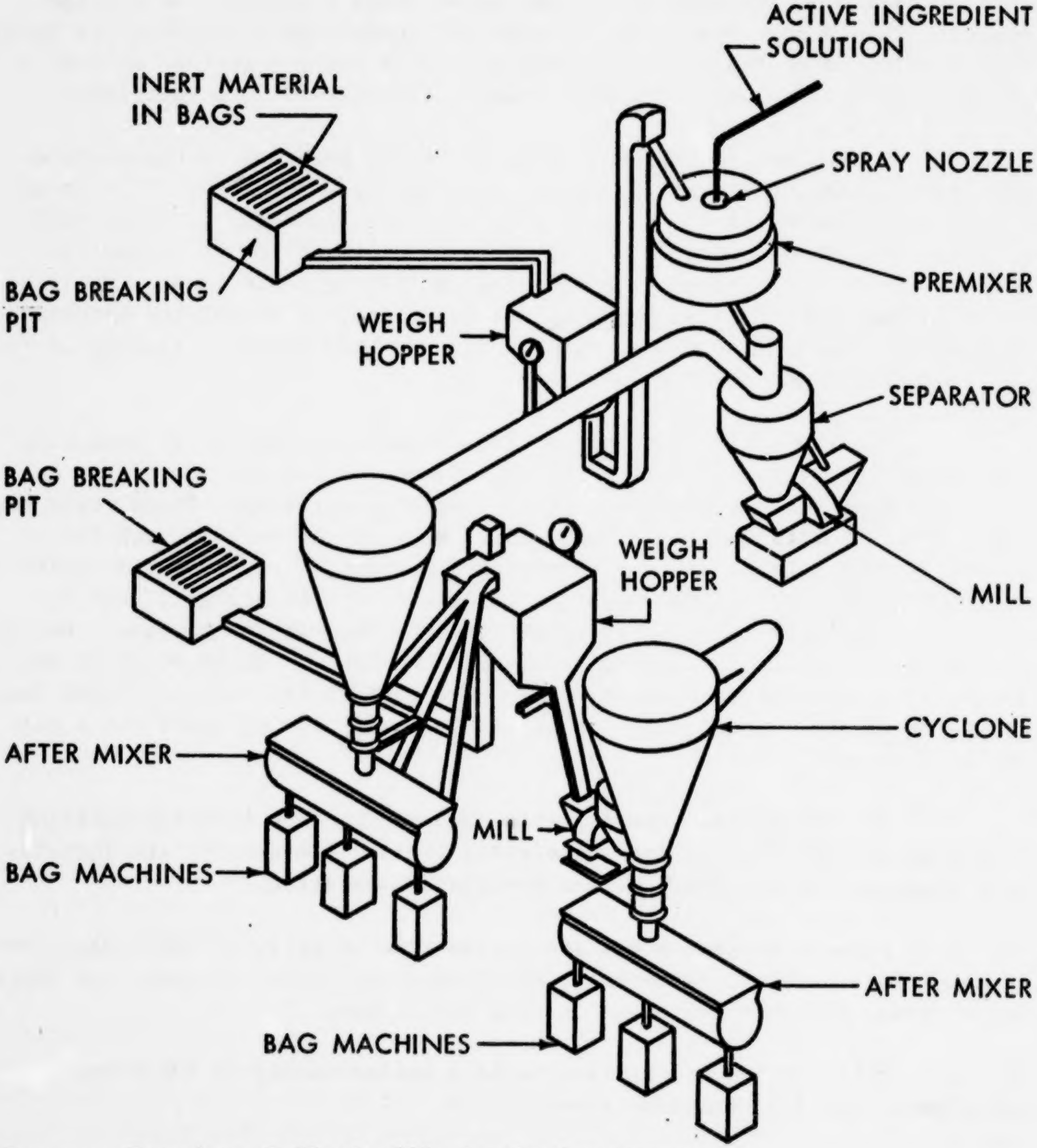
The potential exists for loss of active material to the environment during the formulation process. Open mixing tanks are used in several liquid formulation lines. At most sites visited, however, lids and vent-scrubber systems are used on mixing tanks to minimize losses to the atmosphere. Rupture of formulation equipment or piping could cause a spill of large columns of technical grade active ingredient or formulated material. Many of the formulation plants visited did not have adequate facilities for dealing with this kind of event.

Quality control techniques for formulation plants are generally limited to the analysis of finished formulation for active ingredient content, for specific impurities and for chemical properties. These tests require a very small quantity of material. Many of the methods used for active ingredient analysis are destructive methods, i.e., they deactivate the active ingredients. Sample material in excess of that actually used for analytical tests is normally recycled into the formulation process. Waste generated by the quality control analysis is normally disposed of in the formulation plant waste systems. Thus, the quality control activities found at the pesticide formulation facilities generally do not represent a pollution potential.

3. Packaging: The finished formulations are normally packaged in facilities adjacent to the formulation lines. Frequently, the formulation step and filling step are one integrated operation.

Formulated pesticides are filled into an array of containers, including glass bottles, paper bags, metal cans and drums, cartons, and fiberboard drums, and in a few cases in bulk containers.

Table XX shows the results of a recent survey on these types of containers used for pesticide formulations.


ACTIVE INGREDIENT SOLUTION
INERT MATERIAL IN BAGS
SPRAY NOZZLE
PREMIXER
BAG BREAKING PIT
WEIGH HOPPER
SEPARATOR
BAG BREAKING PIT
WEIGH HOPPER
MILL
CYCLONE
AFTER MIXER
MILL
BAG MACHINES
AFTER MIXER
BAG MACHINES

Source: Toxaphene Bulletin 620, Synthetics Department, Hercules Inc., Wilmington, Delaware

Figure 45 - Dust Formulation Process

TABLE XX

HOW PESTICIDES ARE MOVING TO MARKET[10]

Package/Container Size	Percentage
Wettable Powders	
1 lb	3
2.5 lb	2
3 lb	8
4 lb	37
5 lb	35
10 lb	3
24 lb	2
50 lb	10
Emulsifiable Concentrates	
1 gal.	26
5 gal.	44
30 gal.	15
55 gal.	15
Granules	
4 lb	4
5 lb	8
10 lb	10
20 lb	4
25 lb	4
50 lb	66
80 lb	4

Smaller packages are normally shipped in a master container. Four 1-gal. containers or four 5-lb cans, for example, are frequently packaged in a cardboard case. Small bags are often packaged in a multiwalled baler bag for shipment. The use of master containers permits palletizing shipments and handling with automated equipment. There is also less danger of damage to the actual pesticide container.[10]

The points at which the potential exists for pesticide emissions in the packaging operation are the package filling stations and from leaking containers. Filling stations are normally fitted with hoods and a vent system to remove any spilled material. Leaking containers discovered in the packaging area can be readily emptied back into the filling line. Leaking containers discovered in the packaging plant, however, are rather unusual. The packaging operation, therefore, has only a low potential for pollution.

4. Storage and shipping: Most of the formulated goods are stored for at least a short period at the formulation site. This storage facility may serve as only a staging area for shipping to remote warehouses, or it may be the principal warehouse itself.

The on-site storage facility is most frequently located on the same plant site, and often in the same building or a building adjacent to the formulation plant. Where a number of different products are formulated, the finished goods are segregated, with herbicides generally isolated from other types of products.[11]

Both public and private warehouses are used to store formulated pesticides. Selection of a warehouse to be used differs from company to company, but generally whether or not the facility is heated and equipped with a sprinkler system are considered.[12]

Both truck and rail shipments are used for formulated pesticides, with trucks being used more frequently for local delivery. Less than car or truck load shipments are normally not made from the initial warehouse in the distribution system. Mixed shipments, however, are apparently common after the first one or two phases of shipping.

Leakers during transportation are an ever present problem and potential source of pollution. Frequency of leaking containers is generally much less than 1%.[13] Leaks are most often caused by rough handling during loading and shipping rather than by defective containers.[14]

The potential exists for the release of significant quantities of pesticides to the atmosphere as the result of either a warehouse fire or accidental spillage or leakage during shipment. The National Agricultural Chemicals Association (NACA) has established a nationwide Pesticide Safety Team Network to deal with accidents involving Class B poison pesticides. This cooperative program provides the personnel, equipment, and expertise necessary for efficient clean-up and decontamination. Ten members provide this service on a 24-hr a day basis: Chevron, Shell, Stauffer, Chemagro, Diamond Shamrock, Velsicol, Niagara, Union Carbide, Monsanto, and Dow. Many of the major companies, including many of those who cooperate with the NACA team, independently provide the same type of assistance for accidents involving any of their products.[12,15,16]

Procedures have been developed for dealing with spills or warehouse fires that help minimize possible pollution hazards and exposure of personnel to toxic vapors.[17] (See Appendix B, page 239). Rapid implementation of these procedures will mitigate the effects of a spill or fire to a large extent.

5. Equipment clean-up: Frequently, the same equipment is used to produce a number of pesticide formulations containing different active ingredients, solvents, etc. Great care must be taken not to contaminate one formulation with traces of another pesticide. Contaminants could adulterate or dilute the following batch, leave an illegal residue on crops to which the formulations were applied, or cause chemical degradation of the active ingredient. Prevention of such "cross-contamination" during formulation requires extensive clean-up of the facility between the formulation of different active ingredients. Guidelines for equipment have been developed by the NACA subcommittee on Cross-Contamination to aid formulators.[18/]

Liquid formulation process equipment are generally rinsed with the solvent used in the previous formulation. The number of rinses as well as the quantity of solvent required depends on the specific equipment. Generally, however, from one to five rinses with 20 to 50 gal. of solvent are sufficient to decontaminate most types of equipment. Line strainers, filters, and other points in the system where residues could accumulate must be cleaned. In many cases, the solvent used for rinsing can be saved and used the next time the same product is formulated.

Dry formulation plants generally require flushing with a dry inert material before producing a different product. In many cases, it is possible to save this inert material for use in later production.

If liquid spraying was used on the previous product, a solvent must be used to flush the spray system.

In many cases, it is necessary to disassemble some items of equipment and use mechanical cleaning equipment. Steam and hot water washes are also used.

The material used to clean the equipment is generally handled in one or two ways. It can be temporarily packaged and stored until it can be used the next time the same product is formulated, or it can be treated as a liquid or solid waste, and treated accordingly as discussed in the following section. The pollution potential that exists from equipment clean-up is dependent on the adequacy of the formulation plant's liquid and solid waste treatment system. Material that is packaged and held until it can be used does not represent a significant pollution hazard.

6. Wastes and by-products: By-product and waste production from pesticide formulation facilities is less of a problem than for active ingredient manufacture. There are no major by-products as such, and wastes are primarily limited to empty containers, wrappers, and small volumes of liquid and solid material.

These wastes are treated by almost all of the available means, including incineration, landfill, evaporation, special waste treatment systems, deep wells, and discharge into municipal sewer systems.

The formulation facilities best equipped to handle their wastes are generally those located at the site of active ingredient manufacture. Such a location can recycle waste streams from the formulation activity to either the production facility for recovery or to the production facility's waste treatment system.

Landfill is the method most frequently observed for the disposal of solid wastes. This is normally done by a contract service that picks up the waste at the formulation plant. The ultimate destination of the solid waste is not always known by the pesticide formulator.

Liquid wastes can be effectively handled in some parts of the country by evaporation ponds.[5,19-21] Ponds of this type have been used for several years without having to remove accumulated sludge.[20] Atmospheric emissions of active ingredients from this type of system, however, have apparently not been determined.

The problem of how to adequately handle liquid wastes has resulted in a concentrated effort to minimize liquid waste production. Washdowns of equipment and facilities are kept to an absolute minimum. Industrial vacuum cleaners are used to clean up solid material, adsorbents for liquids. Production runs are scheduled to minimize the number of equipment clean-ups necessary. Many formulation facilities have removed or plugged all floor drains.

Discharge data on pesticide formulation facilities were generally not available. However, it appears that there is potential for significant discharge of pesticidal material from some formulation plants.

7. Surplus pesticides: The term surplus pesticides, as is used in this study, encompasses three situations where formulated material is not marketable: (1) formulated material left at the end of the season--truly surplus pesticides; (2) off-specification material; and (3) formulations that can no longer be legally sold--recalled material.

The least troublesome category is that material left over after the growing or use seasons. In most cases, pesticide formulations are stable for extended periods when stored under the proper conditions. Consequently, material left over after the use period is simply stored until needed.

Off-specification batches of material are a fact of life in pesticide formulation as they are for all types of manufacturers. Formulations generally fail to meet specifications for one of two reasons: (1) the wrong concentration of active ingredient; or (2) inadequate physical properties.

Material that is off-specification for these reasons can generally be reworked or blended off without major difficulty. Reference to only one occasion was found where a batch of off-specification material had to be destroyed, and this was because of cross-contamination with DDT.[15] Recent effort by the NACA[18] as well as individual formulators has helped to virtually eliminate cross-contamination as a major problem.

Recalled material has been a serious problem for some formulators.[22] The 15 April 1970 suspension of several registrations for liquid 2,4,5-T formulations is a classic example. This announcement resulted in an attempt by over 100 formulators to recall 6,000,000 containers of over 300 products from more than 200,000 retail outlets. The most difficult problem in dealing with recalled material, however, was how to adequately dispose of it after it has been collected. One company was reported to have accumulated 44,000 gal. of a 1% 2,4,5-T formulation. This volume of unwanted pesticidal material certainly has potential for environmental damage.

8. Empty containers: Empty active ingredient containers are a problem. Pesticide formulators generally solve this problem in one of two ways: (1) reuse of the containers; or (2) burial.

Many fomulators reuse incoming active ingredient containers (primarily 55-gal. drums) for formulations that contain the same active ingredient. This practice not only eliminates his immediate problem of container disposal, but also reduces the overall number of empty containers to be dealt with. Formulators who service a local market are also able to recycle drums and use them in the same service for three to six cycles.[20]

Many 55-gal. drums can be reconditioned and reused for other purposes. The reconditioning procedure normally includes preliminary decontamination, firing to about 1200°C, reshaping, sand-blasting and repainting.

Nonreusable containers are most frequently disposed of by landfill. Thus, after being crushed, these empty containers become part of the solid waste from the formulation plant.

The potential exists for environmental damage from empty active ingredient containers if they are not properly disposed of. One major active ingredient manufacturer requires as a part of his contract with the formulator that a certificate of disposal for all containers be submitted.[14/] Only disposal methods approved by the basic manufacturer are accepted.

9. Safety practices: Two general categories of safety equipment and practice are found in industry: (1) those designed specifically for personnel protection, and (2) control devices used to contain and control potentially toxic or polluting substances.

Personnel safety standards observed in pesticide formulation plants are less stringent than those found in active ingredient plants. Standard industrial safety equipment, including rubber gloves, aprons, and various types of respiratory devices are generally available. Use of these items, however, is apparently not always enforced.

Control devices used include baghouses, vent systems, and scrubbers. Generally, more sophisticated and efficient devices are used whenever highly toxic pesticides are formulated.

Perhaps the greatest pollution potential associated with the safety aspects of pesticide formulation is the lack of adequate contingency plans for handling fires or explosions. Detailed procedures for handling pesticide warehouse fires have been outlined[17/] and are generally applicable to formulation plants. Preexisting plans to implement these procedures, however, are apparently uncommon among pesticide formulators.

LITERATURE REFERENCES

1. Eichers, Theodore R., Liquid Pesticides: Formulation and Distribution by Two Southern Cooperatives, U. S. Department of Agriculture, Washington, D. C., 1965.
2. Personal communication from Mr. Don Gohlson.
3. Personal communication from Dr. J. B. Moore.
4. Day, Hurbert M., "Report of Review Committee of Chemical Specialties Manufacturers Association," presented at the National Working Conference on Pesticide Disposal, Beltsville, Maryland, 30 June and 1 July 1970.
5. Personal communication from Mr. Phil Henery.
6. Anon., "Mercury Containing Pesticides Licensed in 1967," Environment, Vol. 11, No. 4, pp. 6-7, May 1969.
7. Raw, G. R., Ed., CIPAC Handbook, Vol I: Analysis of Technical and Formulated Pesticides, National Agricultural Chemists Association, Washington, D. C., 1970.
8. Dawson, G. W., A. J. Shuckrow, and W. H. Swift, Control of Spillage of Hazardous Polluting Substances, Department of the Interior, Washington, D. C., 1970.
9. Personal communication from Transamerica Trucking Company.
10. Anon., "What Pesticide Formulators Say About Packaging," Farm Chemicals pp. 62-68, September 1968.
11. Personal communication from Mr. Willis H. Hart.
12. Personal communication from Mr. Joe W. Gillespie.
13. Personal communication from Mr. Bud Schroeder.
14. Personal communication from Mr. Tom J. White.
15. Personal communication from Mr. James H. Vines.
16. Personal communication from Mr. J. H. Bees.

17. Cenner, James T., "Report of the National Agricultural Chemical Association," presented at the National Working Conference on Pesticide Disposal, Beltsville, Maryland, 30 June and 1 July 1970.

18. *Prevention of Cross-Contamination of Pesticide Chemicals*, National Agricultural Chemicals Association, Washington, D. C., 1965.

19. Personal communication from Mr. Max Sobelman.

20. Personal communication from Mr. E. A. Gilbert.

21. Personal communication from Mr. Darol Lloyd.

22. Hill, Ralph M., "Recall and Disposal," presented at the National Working Conference on Pesticide Disposal, Beltsville, Maryland, 30 June and 1 July 1970.

VI. MARKETING OF PESTICIDES

The marketing of pesticides constitutes a number of activities which, in total, compose a large segment of commerce. As used herein, marketing will be used to cover the movement of finished pesticidal goods from the manufacturer, formulator or packager into the hands of the actual consumer. Separate activities include transportation, warehousing, redistribution and storage or shelving at the point of purchase. The evaluation of the pollution potential associated with pesticide marketing activities is made extremely difficult by the multiplicity of pathways utilized in getting the manufactured active ingredient to the consumer.

The nearly 100 domestic manufacturers[1,2/] of pesticides and related products utilize widely varying systems for distributing or selling their products--some may sell directly to the consumer while most work through various chemical companies, formulators, packagers, distributors, brokers or retailers. A considerable amount of the manufactured pesticides moves through the hands of possibly as many as 500 independent formulators and an unknown number of packagers including over 20 aerosol packagers. Many of these formulators and packagers have their own label registrations, market their own products, and are frequently listed as manufacturers: e.g., mailing lists[3/] indicate 68 DDT manufacturers and distributors, 68 weed-killer manufacturers, 647 insecticide manufacturers, 639 disinfectant manufacturers, 5,545 manufacturers of agricultural chemicals, and 9,632 chemical manufacturers of all kinds (although only about 600 producers of synthetic organics of all kinds were listed by the tariff commission[4/]). On the other hand, many of the manufacturers and formulators do not market directly to the consumer at all. The movement of pesticides from producer to consumer can be summarized by the seven routes shown below:

Movement of Pesticides From Manufacture to Consumer

1. Manufacturer Direct
2. Distributor to Dealers
3. Area or Regional Distributors--to distributors to dealers
4. Manufacturer's Agents
5. National Distributors
6. Co-Manufacturers
7. Formulator--Distributors

The total number of outlets varies widely for different pesticides, depending on their properties, application patterns, and company marketing programs, ranging from hundreds of thousands of outlets for pyrethrum-containing products to very few for the extremely toxic sodium fluoroacetate, which is used only by certain professional applicators. The number of outlets is not available for each pesticide (or for almost any pesticide), but estimates have been made according to the type of business involved relying on mailing list information[3/] as shown in Table XXI.

Some overlap occurs between some categories, but one can conservatively estimate that the United States has 30,000 locations handling lawn and garden, home (excluding aerosols), industrial and structural pesticides, i.e., excluding large-scale agricultural or land management usages. The number of outlets for agricultural pesticides is smaller, but one herbicidal product (alachlor, which is used primarily on midwestern corn and soybeans) was estimated[6/] to be available on "about 15,000 shelves." Agricultural pesticides in general probably fall in the range of 100 to 20,000 outlets each. Good data on the pesticide losses during the various marketing activities are nonexistent. As a minor task of this program, different methods of estimating losses were made, based on the data in Table XXI, the literature, and an informal survey of local pesticide handlers.

Losses would occur during transporation, from the formulator to the wholesaler or retailer, in handling and warehousing, and at the place of sale to the consumer, or point of export. The total amount of pesticides of all kinds produced and sold in the United States averages about 1 billion pounds per year. An estimate of 0.1% loss from all sources during marketing would mean losses of 1 million pounds per year. This estimate is probably too large, but may serve as an upper limit. An estimate of 0.01% may be realistic and would mean 100,000-lb loss.* The actual number may be less significant than the methods used to handle the losses--for example, effective detoxification is probably not practiced for spills at these points as they would be in the plant of the experienced manufacturer or formulator. In addition, technically untrained drivers, warehousemen, stock boys or janitors may be exposed to hazardous spills.

The home and garden market for pesticides is a sizable segment of the industry--perhaps as large as 20% of the total. Over 100 chemicals are said[8/] to be used in this market and are marketed as many hundreds of finished products. Major pesticides by use category are shown in Table XXII. These products are normally marketed in small containers as shown[8/] in Table XXIII. The total number of containers is uncertain, but about 100 million units of pesticides in aerosol containers are sold annually, most of which goes to the home and garden market. The aerosols are the largest single type of container and one might assume that the total number of containers is in the range of 200-500 million.

---

* The loss at the marketing level would actually include much formulated or diluted product whereas the 1 billion pounds production figure refers largely to the technical (concentrated) product.

TABLE XXI

MARKETING OUTLETS TO THE CONSUMER FOR PESTICIDES

Major Agricultural Outlets	
Manufacturers	40 (estimate)
Formulators	300 (estimate)
Distributors, independent	100 (estimate)[a]
Farm Cooperatives	3,640 of the 8,090 Co-Ops are said to handle agricultural chemicals[b]
Feed and Grain	27,904 (10,108 grain elevators are also listed)
Fertilizer Retailers	8,905
Specialized Outlets	
Structural Pest Control	23 members of United Pesticides Formulation and Distributors Association sell to structural pest control operators[b]
Turf Pest Control	110 distributors sell primarily to professional golf course applicators
Household Pest Control	540 members of the Chemical Specialties Manufacturers Association are engaged in production and marketing of chemicals for household use
Others	Not available
Home and Garden Market	
Gardener's Supplies	7,919 firms
Two Categories of Firms Which Frequently Handle a Wide Range of Pesticides	
Hardware Retailers	28,297
Department Stores	1,500 of the 11,580 department stores are estimated to have garden centers[c]
Six Categories Which Handle Smaller Amounts or Selected Lines of Pesticides	
Lumber and Wood Builders Supplies	20,602 retailers
Drug Stores	48,869 total (11,200 rated at $50,000 per year)
Discount Stores	4,888 retailers
Industrial Supplies	7,500 wholesalers
Janitor Supplies	5,000 dealers
Nurseries	1,600 estimated large mail order firms of the 31,885 total
Three Categories Which Primarily Serve the Home-Use Market, Particularly Aerosols	
Grocery Stores	75,000 supermarkets of the 220,000 retail grocers
Variety Stores	22,708 retailers
Sporting Goods Stores	13,000
Other Categories Which May Carry Pesticide Lines	
Chemical Exporters	513

---

a/ Based on distributors and dealers listed under agricultural chemicals by Ref. 7.

b/ The National Pest Control Association has over 1,220 member companies engaged primarily in structural pest control and is said to account for about 50% of that industry's business.

c/ Montgomery Ward has about 580 and Sears has nearly 400 retail stores in the United States.

TABLE XXII

MAJOR PESTICIDES SOLD IN THE GARDEN AND HOME MARKET[8/]

Insecticides

Aspon
Allethrin
Aramite
Aldrin
BHC
Chlordane
Ciodrin
Diazinon
Dibrom
Disyston
DDT
Dieldrin
Dimethoate
Dimetilon
DDVP
Ethion
Guthion
Heptachlor
Kelthane
Kepone
Lethane
Lindane
Lead Arsenate
Malathion
Meta-Systox
Metaldehyde
Methoxychlor
Naptha
Nictone
Sulfate
Oils
Pyrethrum
Para Dinitrobenzene
Piperonyl Butoxide
Rotenone
Ronnel
Sevin
Sulfur
Tedion
Toxaphene
TDE
Trithion

Rodenticides

Cumarin
Diphacin
Warfarin

Herbicides

Amiben
Amitrol
Ammonium Sulfamate
Benefin
Bensulide
Cacodylic Acid
CIPC
Dalopon
Dacthal
Dicamba
Dichlobenil
Diphenamid
DSMA
Endothall
EPTC
MCPP
Metham
Paraquat
PCP
Sesone
Siduron
Silvex
Trifluralin
Terbutol
TCA
2,4-D
2,4-DB
2,4,5-T
Pramitol
Erbon
DAMA
AMA

TABLE XXIII

TYPES OF CONTAINERS USED FOR GARDEN AND HOME PESTICIDES[8]

	Constructions						
Sites	Paper Bags	Plastic Bags	Glass	Other Plastic	Cardboard[a] Carton & Can	Nonpressurized Metal	Aerosol[b]
4 oz			X	X		X	X
8 oz			X	X		X	X
Pint			X	X		X	X
Quart			X	X		X	
Gallon			X	X		X	
Over gallon				X		X	
1/2 lb	X	X			X		
1 lb	X	X			X		
1-5 lb	X	X			X		
5 lb and over	X	X					

---

[a] Odor barriers may be part of bag, carton, and can construction. These barriers are generally various plastic laminations or foil.

[b] Aerosols vary more in size than other containers and may be sold in odd ounce sizes such as 22 oz.

The lawn and garden portion of the total home and garden market is somewhat narrower in the number of pesticides involved and probably much narrower in terms of the number of outlets. About a dozen local retail and wholesale lawn and garden centers were surveyed. They said that they experience breakage or spillage of one or two containers each per year, but in some cases part of the contents can be salvaged. We estimate an average loss of about 5-10 lb/year/center. If we assume there are 10,000 major lawn and garden centers, then the total estimated loss is about 75,000 lb/year.

The remainder of the home and garden market would in general utilize smaller containers and based on the estimate for lawn and garden we would estimate the total home and garden loss during marketing as less than 100,000 lb/year of formulated products. These contain generally much lower than average amounts of active ingredient--perhaps 10-20%.

The agricultural market is by far the largest segment of the pesticide industry with perhaps 500 pesticidal chemicals and 50,000 formulations marketed. The container size averages larger than those in the home and garden market as does also the content of active ingredient. Estimates of the number of units (containers) of pesticides sold to farmers for uses on crops, livestock, etc., range from 91[8] to 134 million[9] for 1966. The average container was estimated to contain about 8 lb total of which about half was active ingredient. The distribution according to container size and use is shown in Table XXIV.

Evaluation of the losses of pesticides during marketing to agricultural uses is hindered by a good estimate of the number of outlets. The 3,640 farm cooperatives in the United States which handle agricultural chemicals account for a large share of pesticide sales: 32% for the Co-Ops vs. about 15% for the lawn and garden centers. (Some of the Co-Ops also formulate, but this activity is not included here.) Neglecting for the present that the Co-Ops handle larger-size containers on the average than the lawn and garden centers, and assuming that losses are proportional to the amount sold, one would estimate losses of about 160,000 lb/year. However, if losses at the Co-Op average 20-25 lb/year, then a total loss of about 80,000 lb/year occurs.

The total loss for all agricultural outlets may run as high as 200,000 lb/year during marketing activities.

Another sizable segment of the pesticide industry is the structural use and the professional applicator. No estimates have been found for the number of containers or average container size for these general areas. The number of containers used is probably smaller than either of the two previous categories considered--perhaps 5-10 million--but the average size and content of active ingredient is probably larger--possibly 10 lb and 65%. Losses during marketing are probably very small because of the more direct-order nature of the business.

TABLE XXIV

NUMBER AND TYPES OF CONTAINERS FOR AGRICULTURAL AND RELATED PESTICIDE USE[9]

(Million Containers)

Size of Container[2]	Unit	Crop				Noncrop				
		Herbicides	Insecticides	Other Crop Pesticides	All Crop Pesticides	Livestock	Stored Crops	Seedbeds and Transplants	Total	Rodent Control
Dry containers:[3]										
Less than 3	Pounds	0.1	1.1	0.1	1.3	1.3	0.1	0.1	1.5	
3 to 6	Pounds	2.7	21.0	1.3	25.0	1.1	0.2	0.2	1.5	
7 to 10	Pounds	1.0	2.1	-	3.1	1.1	0.7	0.7	2.5	
11 to 20	Pounds	0.4	0.5	-	0.9	-	0.1	0.1	0.2	
21 and over	Pounds	1.6	4.8	0.1	6.5					
Total dry containers	Number	5.8	29.5	1.5	36.8	3.5	1.1	1.1	5.7	
Liquid containers:[5]										
1 pint	Pints	20.1	2.8	0.4	23.3	0.4	0.1	-	0.5	
1 quart	Quarts	1.5	13.3	1.5	16.3	1.8	0.1	0.1	2.0	
1 gallon	Gallons	0.1	0.1	0.2	0.4	1.6		0.1	1.7	
5 gallons	Gallons	0.2	0.1	0.3	0.6	0.4			0.4	
30 gallons	Gallons	0.1		0.1	0.2					
55 gallons	Gallons	0.1		0.1	0.2					
Total liquid containers	Number	22.1	16.3	2.6	41.0	4.2	0.2	0.2	4.6	
Total containers	Number	27.9	45.8	4.1	77.8	7.7	1.3	1.3	10.3	3

Note: Total pesticides containers: 91.1 million.

Contacts with local firms regarding pesticide losses in transportation and warehouse handling indicate that records are not kept, although Hazardous Materials Incident Reports are filed as required by the Department of Transportation. Losses may total twice that in the lawn and garden centers or 150,000 lb/year. The total for the three phases of marketing would then be on the order of 450,000 lb/year or 0.04% of the pesticides produced. Discussions with local pesticide handlers regarding clean-up procedures in event of spills or breakage indicate that much of this estimated 300,000 lb would be washed into city sewers, disposed of with other solid wastes or perhaps thrown on the ground.

LITERATURE REFERENCES

1. "Pesticides and Related Products, 1970," United States Tariff Commission, Washington, September 1971.

2. Neumeyer, J., D. Gibbons, and H. Trask, "Pesticides," Part I and II, Chemical Week, pp. 38-68, 12 April, and pp. 38-68, 26 April 1969.

3. 1971-1972 Hofheimer Catalog of United States and Canadian Mailing Lists, Fritz S. Hofheimer, Inc., New York.

4. "Synthetic Organic Chemicals 1969," United States Tariff Commission, Washington, 1971.

5. Personal Communication, Mr. Joseph Gillispie, Monsanto Company, 11 October 1971.

6. Personal Communication, Dr. Bernard Sanders, Farmland Industries, September 1971.

7. Farm Chemicals Handbook-1971, Meister Publishing Company, Willoughby, Ohio.

8. Day, H. M., "Report of Study Committee-Chemical Specialties Manufacturers Assocations," presented at The National Working Conference of Pesticide Disposal National Agricultural Library, Beltsville, Maryland, 30 June - 1 July 1970.

9. Davis, V. W., "Farmer's Use of Pesticides and Pesticide Containers," presented at The National Working Conference on Pesticide Disposal National Agricultural Library, Beltsville, Maryland, 30 June - 1 July 1970.

10. Jansen, L. L., "Estimates of Container Numbers by Size, Type and Formulation Involved," presented at The National Working Conference on Pesticide Disposal National Agricultural Library, Beltsville, Maryland, 30 June - 1 July 1970.

VII. CONCLUSIONS AND RECOMMENDATIONS

The use of pesticides plays an important role in the health and economy of the United States, but this use is also a cause of much concern over the contamination of the environment and the unbalancing of delicate ecosystems. The industrial and commercial enterprise, which exists to make these pesticides available to the consumer, comprises a large network of activities including synthesis, testing, production, formulation, packaging, transportation, warehousing, and marketing at many levels. Accompanying these activities are numerous points at which pesticides and related hazardous materials can be discharged, emitted, disposed, spilled or otherwise released to endanger man and the local or global environment. The evaluation of the pollution potential of these sources is hindered in many areas by the unavailability of good information. In this study we have attempted to evaluate this potential and have reached a number of conclusions:

1. The unavailability of data on how much of each pesticide is produced or even which ones are produced in the largest quantities is a serious handicap. This information is in the hands of the United States Tariff Commission, but is not disclosed in a meaningful manner because of confidential nature of production data. We recommend that disclosure of production data for pesticides and all hazardous materials be made mandatory so that the public can use these data to evaluate environmental danger.

2. The major pesticide producers have, on the whole, extensive wastewater treatment facilities. Many of these are new or newly-modified and many are under construction or in design, but some still have little or no effective treatment procedures at some facilities. The disposal of liquid wastes from pesticide manufacture varies widely with different companies, different products, and different geographical locations. Methods being used include: many varieties of neutralization, oxidation, settling, and holding ponds and also secondary and biological waste treatment plants (all of which are followed by discharge to a stream or lake); evaporation basins (which have no outfall); deep well disposal; deep ocean disposal; and incineration. Unfortunately, data on the discharge of effluents to navigable waters is only beginning to become available under the "1899 Refuse Act," for disposal of materials into navigable waters. Pesticide producers were scheduled to submit discharge data to the Corp of Engineers at a time when this study was nearing completion and very little data became available in time to be evaluated. Preliminary review, however, indicates that production processes as presently employed for several product lines do lead to sizable losses of active ingredients, toxic raw materials, by-products, etc., and that these are often not detoxified by the waste treatment facilities. On the other hand, this study has found that the major persistent chlorinated hydrocarbon insecticides are now produced in facilities which do not discharge liquid wastes to a river, i.e., they are using evaporative basins, deep well, etc.

3. The production processes have numerous potential sources of pollution in addition to the primary liquid waste streams, including air emissions, solid wastes, and miscellaneous liquid wastes. The major producers appear to be cognizant of these sources and exercise controls to satisfy local requirements. In a number of cases solid or liquid wastes containing active ingredients go to approved landfills or other burial sites without detoxification, e.g., a liquid waste which apparently contains DDT goes to an approved Class 1 dump in California. At a few facilities high efficiency incinerators are used to dispose of such wastes and we recommend this practice.

Data on air emissions of pesticides are not yet available from production plants and are much in need. The major producers have expended much effort to install baghouses, scrubbers, and other air pollution controls; but data on loss of active ingredients through these devices are needed.

4. Some of the biggest sources of pollution from the major manufacturers are not from the active ingredient (i.e., the pesticide) but from unrecovered by-products such as H_2S which may be flared to SO_2: e.g., a plant which produces 10 million pounds per year of most thioorganophosphates could emit over 2 million pounds of SO_2 which would compare with that emitted from a small electric power plant. In addition, and depending on the fuel used for process heat and the air pollution controls installed, such a plant might well produce 5 to 10 million pounds per year of particulate pollutants (fly ash, etc.). By comparison, the amount of active ingredient discharged through the waste treatment plant would probably be less than 10,000 lb/year.

5. Numerous examples were noted wherein companies have recently modified their production and waste disposal facilities to decrease the amounts of wastes generated or lost; e.g., improved recycle; recovery and decontamination of by-products; use of lined settling basins to avoid seepage, etc.

Most of the production equipment is dedicated to one product or to two very similar products so that cleaning wastes are minimal.

A host of smaller potential pollution sources were noted, some of which have received attention by some producers, but not by others, e.g.; carry-out of pesticides on shoes and clothes are prevented by sending company-provided work-wear along with wipe cloths, etc., to special laundries, followed by recycle or detoxification of the wash liquid; wash basin or lavatory wash water is sent to the waste treatment plant rather than discharged with sanitary wastes; and the proper disposal of "bottoms" from solvent recovery operations.

6. The formulation of pesticides is probably a larger source of environmental pollution than is the initial production. The formulation is

done in some cases by the manufacturer at the production site, but in most cases it is not. A host of formulators process hundreds of pesticides into thousands of finished products. By the nature of this arrangement many of the formulators have relatively small facilities and many of the formulation runs are relatively short. The combined result is that formulators with few exceptions have less extensive waste treatment facilities than do the manufacturer, but they generate considerably more wastes from equipment clean-up. However, the majority of the forulators probably send liquid wastes to municipal sewer systems so that no data are becoming available on the amounts discharged. These smaller businesses are also more apt to send pesticide-containing solvents to commercial solvent reclamation services (where the fate of the pesticide is uncertain) than is the manufacturer.

7. The transportation of pesticides, as with many other products, causes increased chances of accidental breakage, spills and losses. The potential for environmental damage is higher in the case of concentrated active ingredient than it is with more dilute formulated products, but the frequency of accidental occurrences varies widely with packaging and shipping practices. Overall, the pesticide industry has had relatively few major spills, but the potential remains inherent in the transportation of hazardous materials.

Of smaller scope, but of importance we believe, is the increased pollution potential of tank trucks over railroad tank cars in regard to clean-out procedures; cars are frequently dedicated, require only occasional clean-out, and this is done at the manufacturer's site with wastes going to treatment; the trucks are most often leased one-way and are cleaned by the operator at a point remote from detoxification facilities.

Another important pollution point related to the need to transport pesticides is the inability to empty the standard 5- and 55-gal metal drums completely. These drums may often be reused for formulated products, etc., and losses at the manufacturer/formulator/packager level are not nearly so large as those at the consumer level; but new designs are needed which permit complete drainage.

8. The warehousing and marketing of pesticides are a smaller source of pollution, but losses in this area are frequently disposed to the nearest sewer or trash can.

9. Overall the environmental impacts from pesticide manufacturing/formulating/packaging/marketing activities appear to be small compared to those resulting from consumer use of these products, but those negative impacts of the former activities have zero benefit/cost ratios and should be minimized.

APPENDIX A

TOXICITY DATA ON SELECTED PESTICIDES[1,2]

I Herbicides and growth regulants

	Oral LD$_{50}$ [3] mg/kg	Dermal LD$_{50}$ [3] mg/kg
Acrolein	42-46	562 Rb
Allidochlor (CDAA, Randox®)	700	360
Ametryne (Gesapax®)	1110-2980	
Amiben (Chloramben®)	3500-5620	3136 Rb
Aminotriazole (Amitrole®)	1100-2500	>10,000
Ammonium sulphamate (Ammate®)	3900-4400	
Arsenites, Na/K	70	150
Asulam	>5000	
Atratone	1465-2400	
Atrazine (Gesaprim®)	2000	
Avadex® (Di-allate)	393-1000	2000-2500 Rb
Avadex BW® (Tri-allate)	800-1810	
Azak® (Terbutol)	>34,600	>10,250
Balan® (Benefin, Quilan®)	>10,000	
Banvel-D® (Dicamba)	1100	>1000
Banvel-T® (Tricamba)	300-450	>1000
Barban (Carbyne®)	600	>1600
Benazolin	>3000	
Benefin (Balan®, Quilan®)	>10,000	
Bensulide (Betasan®)	770-1910	2000->9400 Rb
Benzthiazuron (Gatnon®)	1280	>500
Betanal® (Phenmedipham)	>2000	>500
Betasan® (Bensulide)	770-1910	2000->9400 Rb
BIPC (Chlorbufam)	2500	
Borates	2000-5330	
Bromacil (Hyvar-X®)	5200	
Bromoxynil	190-260	
Cacodylic acid	1350-3200	
Carbyne® (Barban)	600	>1600
Casoron® (Dichlobenil)	2700-6000	1350 Rb
CDAA (Allidochlor, Randox®)	700	360
CDEC (Sulfallate, Vegadex®)	850	
Chlorthal-methyl (DCPA, Dacthal®)	>3000	>10,000 Rb
Chloramben (Amiben)	3500-5620	3136 Rb
Chloranocryl (Dicryl, DCM)	3160	>3160 Rb
Chlorates, Na/K	1200-7000	
Chlorazine	1950	
Chlorbromuron	4287	
Chlorbufam (BIPC)	2500	
Chlorfenac (Fenac®)	1780-3000	>1360 Rb

	Oral LD$_{50}$ [3] mg/kg	Dermal LD$_{50}$ [3] mg/kg
Chlormequat chloride (ccc)	670	232-440 Rb
Chloroxuron (Tenoran®)	3700	>10,000 Rb
Chlorpropham (CIPC, Chloro-IPC)	3800-8000	
Chlorthiamid (Prefix®)	757	1000
CIPC (Chlorpropham, Chloro-IPC)	3800-8000	
CMPP (Mecoprop, Isocornox®)	700-1500	
CMU (Monuron)	3600-3700	>2500 Rb
Clobber® (Cypromid)	215-900	3038 Rb
Cotoran® (Fluometuron)	8900	>10,000 Rb
Cycluron (OMU)	1500-2600	
Cypromid (Clobber®)	215-900	3038 Rb
2,4-D	400-500	1500
Dacthal® (Chlorthal-methyl, DCPA)	>3000	>10,000 Rb
Dalapon-Na	4000-9300	
Daxtron® (Pyriclor)	80-130	>2000
Dazomet (DMTT®, Mylone®)	320-1000	>1000 Rb
2,4-DB	700	800
DCM (Chloranocryl, Dicryl)	3160	>3160 Rb
DCPA (Chorthal-methyl, Dacthal®)	>3000	>10,000 Rb
DCU (Dichloral urea)	6800	
DEF	325	
2,4-DEP	850	
2,4-DES-Na (Sesone, Disul)	700-1400	
Desmetryne (Semeron®)	1630-2375	>1000
Di-allate (Avadex®)	393-1000	2000-2500 Rb
Dicamba (Banvel-D®)	1100	>1000
Dichlobenil (Casoron®)	2700-6000	1350 Rb
Dichlone (Phygon®)	1300-2250	
Dichloral urea (DCU)	6800	
Dichlorprop (2,4-DP)	800	1400
Dicryl (Chloranocryl, DCM)	3160	3160 Rb
Dimexan	240-340	
Dinitrocresol (DNOC)	25-40	200-600
Dinoseb (DNBP)	50	80-200
Dinoterb-acetate	62	
Diphenamid	700-1050	>2000 Rb
Diphenatrile	3500	
Diquat dibromide (Reglone®)	400-440	>500 Rb

1/ Jones, K. H. et al., "Acute Toxicity Data for Pesticides (1968)", _World Review of Pesticides_ (Autumn, 1968).

2/ Neumeyer, John, et al., "CW Report Pesticides", Parts I and II. _Chemical Week_ (April 12 and 26, 1969).

3/ LD$_{50}$ in rats except where noted for rabbits (Rb).

	Oral LD$_{50}$ 3/ mg/kg	Dermal LD$_{50}$ 3/ mg/kg
Disul (2,4-DES-Na, Sesone)	700-1400	
Diuron (Karmex®)	3400-3700	
DMPA (Zytron®)	270	
(DMTT®, Dazomet, Mylone®)	320-1000	>1000 Rb
DNBP (Dinoseb)	50	80-200
DNOC (Dinitrocresol)	25-40	200-600
2,4-DP (Dichlorprop)	800	1400
DSMA	1800-2800	
Endothal	80	750
EPTC (Eptam®)	1600-3160	1460-10,000 Rb
Erbon	1120	
EXD (Herbisan®)	603	
Fenac® (Chlorfenac)	1780-3000	>3160 Rb
Fenoprop (Silvex®, 2,4,5-TP)	650-1070	
Fenuron	6400-7500	
Fluometuron (Cotoran®)	8900	>10,000 Rb
G 36393 (Methoprotryne, Gesaran®)	>5000	>150
Gatnon® (Benzthiazuron)	1280	>500
Gesagard® (Prometryne)	2500	>1000
Gesapax® (Ametryne)	1100-2980	
Gesaprim® (Atrazine)	2000	
Gesaram® (Methoprotryne, G 36393)	>5000	>150
Gesatop® (Simazine)	5000	
Glytac®	7000	
Gramoxone® (Paraquat dicloride)	112-200	236-500 Rb
Herban® (Noruron, Norea)	1476-4000	
Herbisan® (EXD)	603	
Hydram® (Molinate, Ordram®)	501-720	>2000 Rb
Hyvar® (Isocil)	3400	
Hyvar-X® (Bromacil)	5200	
Ioxynil	100-305	
IPC (Propham)	1000-9000	
Isocil (Hyvar®)	3400	
Isocornox® (Mecoprop, CMPP)	700-1500	
Karmex® (Diuron)	3400-3700	
Lenacil (Venzar®)	>11,000	
Linuron	1500-4000	
Maleic hydrazide	3800-6800	>4000 Rb
MCPA	800	>1000
MCPB	680	1000
Mecoprop (CMPP, Isocornox®)	700-1500	
Medinoterb-acetate	42	
Merphos	1270	
Metabromuron (Patoran®)	2000-3000	>10,200 Rb
Metham-Na (Vapam®)	820	800 Rb
Methiuron (Thiuron)	2200	
Methoprotryne (G 36393, Gesaran®)	>5000	>150
Molinate (Hydram®, Ordram®)	501-720	>2000 Rb
Monalide	>4000	
Monochloracetates	300-400	

	Oral LD$_{50}$ 3/ mg/kg	Dermal LD$_{50}$ 2/ mg/kg
Monolinuron	1800-2250	
Monuron (CMU)	3600-3700	>2500 Rb
Morfamquat Dichloride (PP 745®)	368-800	
Mylone® (Dazomet, DMTT®)	320-1000	>1000 Rb
Naptalam (NPA)	1770-8500	
Neburon	>11,000	
Nitralin	>2000	
Nitrofen	3050	
Norea (Noruron, Herban®)	1476-4000	
Noruron (Norea, Herban®)	1476-4000	
NPA (Neptalam)	1770-8500	
OMU (Cycluron)	1500-2600	
Ordram® (Molinate, Hydram®)	501-720	>2000 Rb
Paraquat dicloride (Gramoxone®)	112-200	236-500 Rb
Patoran® (Metabromuron)	2000-3000	>10,200 Rb
PCP (Pentachlorphenol)	280	105-350
Pebulate (PEBC, Tillam®)	1020-1120	>3000 Rb
Pentachlorphenol (PCP)	280	105-350
Pentanochlor (Solan)	10,000	>10,000 Rb
Phenmedipham (Betanal®)	>2000	>500
Phygon® (Dichlone)	1300-2250	
Picloram (Tordon®)	8200	>4000 Rb
Planavin®	>5000	>2000
PP 745® (Morfamquat dichloride)	368-800	
Prefix® (Chlorthiamid)	757	1000
Prometon (Prometone)	1750-3000	
Prometryne (Gesagard®)	2500	>1000
Propachlor (Ramrod®)	1200	380 Rb
Propanil (Stam F-34®, Surcopur®)	1300-1384	
Propazine	>5000	
Propham (IPC)	1000-9000	
Pyrazon (Pyramin®)	3300-4200	
Pyriclor (Daxtron®)	80-130	>2000
Quilan® (Benefin, Balan®)	>10,000	
Ramrod® (Propachlor)	1200	380 Rb
Randox® (Allidochlor, CDAA)	700	360
Reglone® (Diquat dibromide)	400-440	>500 Rb
Semeron® (Desmetryne)	1630-2375	>1000
Sesone (2,4-DES-Na, Disul)	700-1400	
Siduron	>7500	
Silvex® (Fenoprop, 2,4,5-TP)	650-1070	
Simazine (Gesatop®)	5000	
Simetryne	1830	
Sinbar® (Terbacil)	>7500	
Sirmate®	1870-2140	570-2500 Rb
Solan (Pentanochlor)	10,000	>10,000 Rb
Stam F-34® (Propanil, Surcopur®)	1300-1384	
Sulfallate (CDEC, Vegadex®)	850	

	Oral LD_{50}[3/] mg/kg	Dermal LD_{50}[3/] mg/kg
Surcopur® (Propanil, Stam F-34®)	1300-1384	
Sutan®	4000	>2000 Rb
Swep	552	2480 Rb
2,4,5-T	300-800	
2,3,6-TBA	1500	>1000
Tenoran® (Chloroxuron)	3700	>10,000 Rb
Terbacil (Sinbar®)	>7500	
Terbutol (Azak®)	>34,600	>10,250
Thiuron (Methiuron)	2200	
Tillam® (Pebulate, PEBC)	1020-1120	>3000 Rb
Tordon® (Picloram)	8200	>4000 Rb
2,4,5-TD (Fenoprop, Silvex®)	650-1070	
Tri-allate (Avadex BW®)	800-1810	
Tribonate®	108	
Tricamba (Banvel-T®)	300-450	>1000
Trichloroacetates	3200-6000	
Trietazine	1750-3800	
Trifluralin	5000-10,000	>200 Rb
Vapam® (Metham-Na)	820	800 Rb
Vegadex® (Sulfallate, CDEC)	850	
Venzar® (Lenacil)	>11,000	
Vernolate (Vernam®)	1780	>9000 Rb
Zytron® (DMPA)	270	

II Insecticides and acaricides other than organophosphates

	Oral LD_{50}[3/] mg/kg	Dermal LD_{50}[3/] mg/kg
Aldicarb (Temik)	.93	5
Aldrin	40-60	>200
Allethrin	680-1000	11,200 Rb
Aminocarb (Metacil®)	30	
Animert® (Tetrasul)	6800->14,700	
Aramite®	4000-6000	
Arprocarb (Baygon®)	83-175	>1000
Binapacryl (Morocide®)	58-225	1350 Rb
Bromodan®	12,900	
Carbaryl (Sevin®)	400	>500
Chlorbenside (Chlorparacide®)	2000-10,000	
Chlordane	283	>1600
Chlordecone (Kepone®)	114-140	>2000
Chlorfenson	2000	
Chlorobenzilate	700-3200	>5000
Chloropropylate	>5000	>150
Chlorparacide® (Chlorbenside)	2000-10,000	
Chlorphenamide	340	
DDD (TDE)	400-3400	>5000 Rb
DDT	300-500	2500
Derris	1500	
Dicofol (Kelthane®)	575->2000	1000-1230
Dieldrin	40	>100
Dilan®	475-4000	6000
Dimetan®	140-150	
Dimethrin	>15,000	
Dimetilan®	25-50	600-700
Dimite®	500	
Dinobuton	140-460	2500-5000
Dithioquinox (Quinomethionate, Morestan®, Forstan®)	1100-3000	>1000
Endosulfan (Thiodan®)	35	74-130
Endrin	3-6	60-120
Eradex® (Thioquinox)	1800-3400	>3000
Fenazaflor (Lovozal®)	240	>1000
Fluoroacetamide	15	80
Forstan® (Quinomethionate, Dithioquinox, Morestan®)	1100-3000	>1000
gamma-BHC (Lindane)	200	500-1000
Genite®	1400-1900	
Heptachlor	40	200-250
Isobenzan (Telodrin®)	5-10	5-30
Isodrin	7-17	23-35
Isolan	12	35-60
Kelthane® (Dicofol)	575->2000	1000-1230
Kepone® (Chlordecone)	114-140	>2000
Lead arsenate	10-100	>2400
Lethane®	90-300	125-250 Rb
Lindane (gamma-BHC)	200	500-1000
Lovozal® (Fenazaflor)	240	>1000
Matacil® (Aminocarb)	30	
Methiocarb (Mesurol®)	100-135	
Methoxychlor	5000-7000	6000->6000
Mirex	600-740	>2000
Mobam®	>234	>6000 Rb
Morestan® (Forstan®, Dithioquinox®, Quinomethionate)	1100-3000	>1000
Morocide® (Binapacryl)	58-225	1350 Rb
Neotran®	5800	>1000 Rb
Nicotine	70	140
o-Dichlorobenzene	500	
Penphene® (Tetrachlorothiophene, TD 183®)	70->80	256 Rb
Perthane®	8170-9340	
Pyethrins	570	>1350->5400
Pyrolan®	50-90	
Quinomethionate (Dithioquinox, Morestan®, Forstan®)	1100-3000	>1000
Rotenone	25-132	>940 Rb
Ryania	750-1200	>4000 Rb
Sevin® (Carbaryl)	400	>500
Strobane®	200-250	>5000 Rb
Sulphenone®	1400-3650	>1000 Rb
(TD 183®, Tetrachlorthiophene, Penphene®)	70->80	256 Rb
TDE (DDD)	400-3400	>5000 Rb
Tedion® (Tetradifon)	5000-14,700	>10,000 Rb
Telodrin® (Isobenzan)	5-10	5-30
Temik®	0-6	2-5
Tetrachlorothiophene (Penphene®, TD 183)	70->80	256 Rb
Tetradifon (Tedion®)	5000-14,700	>10,000 Rb
Tetrasul (Animert®)	6800->14,700	
Thanite®	1600	6000 Rb

	Oral LD$_{50}$ [3/] mg/kg	Dermal LD$_{50}$ [3/] mg/kg
Thiodan® (Endosulfan)	35	74-130
Thioquinox (Eradex®)	1800-3400	>3000
Toxaphene	283	>1000
Tranid®	17	200-400 Rb
Zectran®	15-63	1500-2500

III Organophosphorus insecticides

	Oral LD$_{50}$ [3/] mg/kg	Dermal LD$_{50}$ [3/] mg/kg
Abate®	1000-4000	1370-4000
Amidothion (Thiocron®)	600-660	
Aspon®	1295	
Azinphos-ethyl (Ethyl, Guthion®)	9	280
Azinphos-methyl (Guthion®)	7-13	280
Baytex® (Fenthion)	200	1300
Bidrin®	22-45	225 Rb
Birlane® (Chlorfenvinphos)	10-155	108
Bromophos	3750-5180	>1000 Rb
Butonate	1050	>2000
Carbophenothion (Trithion®)	7-30	800
Chlorfenvinphos (Birlane®)	10-155	108
Chlorthion®	625-1500	1500-4500
Cidial®	200-300	700->1400
Ciodrin®	125	385 Rb
Co-Ral® (Coumaphos)	13-180	860
Coroxon	10	
Coumaphos (Co-Ral®)	13-180	860
Coumithoate (Dition®)	67	>200
Cygon® (Dimethoate)	200-300	700-1150
DDVP (Dichlorvos)	25-30	75-900
Delnav® (Dioxathion)	20-40	350
Demeton (Systox®)	3-5	200
Demeton-methyl (Metasystox®)	50-75	300-450
Demeton-S-methyl (Meta-iso-Systox®)	40	85
Diazinon	300-600	500->1200
Dibrom® (Naled)	430	800-1100
Dicapthon	330-475	800-1250
Dichlofenthion (Nemacide®)	250	
Dichlorvos (DDVP)	25-30	75-900
Dimefox (Terra-Sytam®, Hanane®)	2	2-10
Dimethoate (Rogor®, Cygon®)	200-300	700-1150
Dioxathion (Delnav®)	20-40	350
Dipterex® (Trichlorphon)	650	>2800
Disulfoton (Disyston®)	4	50
Dition® (Coumithoate	67	>200
Dowco 109® (Ruelene®)	460-1000	4000 Rb
Dow ET-14® (Fenchlorphos)	1000-3000	>5000
Dow ET-15®	710	>1000
Dursban®	135-163	2000 Rb

	Oral LD$_{50}$ [3/] mg/kg	Dermal LD$_{50}$ [3/]
Dyfonate®	4-17	147
Ekatin® (Thiometon)	100	>200
Endothion	23	130
EPN	8-17	25-230
Ethion	13-34	1600
Ethoate-methyl (Fitios B-77®)	125	2000
Ethyl guthion® (Azinphos-ethyl)	9	280
Etrolene® (Fenchlorphos)	1000-3000	>5000
FAC 20® (Prothoate)	14-25	100-200
Fenchlorphos (Ronnel, Etrolene®, Dow ET-14®)	1000-3000	>5000
Fenitrothion (Sumithion®)	250-673	1500->3000
Fenthion (Baytex®, Lebaycide®)	200	1300
Fitios B-77® (Ethoate-methyl)	125	2000
Folimat®	50	700
Formothion	400	400-1680
Guthion® (Azinphos-methyl)	7-13	280
Haloxon	900-2000	>6000
Hanane® (Dimefox)	2	2-10
Imidan® (Prolate®)	113-230	>3160 Rb
Kilval® (Vamidothion)	64-100	1160 Rb
Lebaycide® (Fenthion)	200	1300
Malathion	1400-1900	>4000
Mercarbam	15	380
Menazon	1200-1600	>500
Meta-iso-Systox® (Demeton-S-methyl)	40	85
Metasystox® (Demeton-methyl)	50-75	300-450
Metasystox R® (Oxydemeton-methyl)	57	100
Methidathion (Supracide®)	20-48	25-400
Methyl Trithion®	98-200	190-215
Mevinphos (Phosdrin®)	3-5	90
Mocap®	61	26-46 Rb
Morphothion	200	283
Naled ([illegible]vrom®)	430	800-1100
Nemacide® (Dichlofenthion)	250	
Oxydemeton-methyl (Metasystox®)	57	100
Parathion	3-6	4-200
Parathion-methyl	12-16	67
Phenkapton Phenkaptone®	50	>1000
Phorate (Thimet®)	2-3	70-300
Phosalone (Zolone®)	120-170	390
Phosdrin® (Mevinphos)	3-5	90
Phosphamidon	15	125
Potasan®	19-40	300 Rb
Prolate® (Imidan®)	113-230	>3160 Rb
Prothoate (FAC 20®)	14-25	100-200
Pyrazothion	36	
Rogor® (Dimethoate, Cygon®)	200-300	700-1150

	Oral LD$_{50}$[3] mg/kg	Dermal LD$_{50}$[3] mg/kg
Ronnel (Fenchlorphos)	1000-3000	>5000
Ruelene® (Dowco 109®)	460-1000	4000 Rb
Schradan	5	50-100
Sulfotep	1-5	20 Rb
Sumithion® (Fenitrothion)	250-673	1500->3000
Supracide® (Methidathion)	20-48	25-400
Systox® (Demeton)	3-5	200
TEPP	0-5	20
Terra-Sytam® (Dimefox)	2	2-10
Thimet® (Phorate)	2-3	70-300
Thiocron® (Amidothion)	600-660	
Thiometon (Ekatin®)	100	>200
Thionazin (Zinophos®)	9-16	8-15
Triamide	20	
Triamiphos (Wepsyn®)	10-20	1500-3000 Rb
Trichlorphon (Dipterex®)	650	>2800
Trithion® (Carbophenothion)	7-30	800
Vamidothion (Kilval®)	64-100	1160 Rb
Wepsyn® (Triamiphos)	10-20	1500-3000 Rb
Zinophos® (Thionazin)	9-16	8-15
Zolone® (Phosalone)	120-170	390

IV Fungicides

	Oral LD$_{50}$[3] mg/kg	Dermal LD$_{50}$[3] mg/kg
Allisan® (Dicloran)	1500-4040	
Binapacryl (Morocide®)	58-225	1350 Rb
Botran® (Dicloran)	1500-4040	
Captafol (Difolatan®)	4200-6200	>800 Rb
Captan (Orthocide®)	8400	
Chloranil	4000	
Copper salts	700-1000	>1000
Daconil®	>10,000	
Dazomet (Mylone®, DMTT®)	320-1000	>1000 Rb
DCMOD (Plantvax®)	2000	
Dehydroacetic acid (DHA)	500-1000	
Dichlofluanid (Elvaron®)	500-1000	>1000
Dichlone (Phygon®)	1300-2250	
Dichloran (Allisan®, Botran®)	1500-4040	
Difolatan® (Captafol)	4200-6200	>800 Rb
Dinitrotrichlorobenzene	500	
Dinocap (Karathane®)	2000	>9400 Rb
Dithianon	1000-1015	
Dithiocarbamates (Maneb, Zineb, etc.)	1000-8000	>1000
Dithioquinox (Quinomethionate)	1100-3000	>1000
(DMTT®, Dazomet)	320-1000	>1000 Rb
Dodine (Melprex®)	566	>1500 Rb
Dyrene®	2700	
Elvaron® (Dichlofluanid)	500-1000	>1000
Ethylmercuric salts	30	200
Fentin salts (Triphenyl tin salts)	238	450
Folpet (Phaltan®)	>10,000	
Forstan® (Quinomethionate)	1100-3000	>1000
Furidazole (Voronit®)	1100	>1000
Glyodin	6800	
Karathane® (Dinocap)	2000	>9400 Rb
Maneb: see dithiocarbamates		
Melprex® (Dodine)	566	>1500 Rb
Metham-Na (Vapam®)	820	800 Rb
Morestan® (Quinomethionate)	1100-3000	>1000
Morocide® (Binapacryl)	58-225	1350 Rb
Mylone® (Dazomet)	320-1000	>1000 Rb
Olin 1763®	>10,000	
Orthocide® (Captan)	8400	
PCNB (Quintozene)	1650-12,000	
Pentachlorophenol (PCP)	280	105-350
Phaltan® (Folpet)	>10,000	
Phenylmercuric salts	60	
Phygon® (Dichlone)	1300-2250	
Plantvax® (DCMOD)	2000	
Quinomethionate (Dithioquinox, Morestan®, Forstan®)	1100-3000	>1000
Quintozene (Terrachlor®, PCNB)	1650-12,000	
Sulphur	non-toxic	
Terrachlor® (Quintozene, PCNB)	1650-12,000	
Thiram (TMTD®)	375-1000	
Triphenyl tin salts (Fentin salts)	238	450
Vapam® (Metham-Na)	820	800 Rb
Voronit® (Furidazole)	1100	>1000
Zineb: see dithiocarbamates		

APPENDIX B

EMERGENCY PROCEDURES IN EVENT OF FIRE IN A WAREHOUSE CONTAINING PESTICIDES[1]

A. In the event of fire, the following agencies should be notified and the noted information supplied;

1. The Fire Department

    a. Advise of hazards from vapor, smoke and contact through contaminated run-off water on actual contact upon entry into burned out area.
    b. Notify of any explosive nature of solvents or other materials if stored.

2. Notify the Police Department

    a. Block off area from all unauthorized persons.
    b. Advise of necessity for evacuation of neighboring businesses or residential areas of persons in the event smoke or vapors drift into their area.
    c. Advise of danger of contact with run-off water and ask help to prevent persons from contact.
    d. In certain areas where active civil defense organizations are found, police may call on them for assistance.

3. In the event rail cars containing pesticides or solvents are in danger of exposure, railroad personnel should be notified and an effort made to switch the cars out.

4. Public health and pollution control agencies (city, county and state) should be advised of types and quantities of pesticides on hand at time of fire and of disposal and decontamination plans.

5. Notify municipal waste treatment personnel if sewers are in the area. Advise of materials possibly going to sewer either directly or in run-off water so they may check for quantity which can be handled in plant and if necessary shutoff sewer lines if overloaded.

B. Examine area for broken water lines and if there is a possibility of contamination through back-up, shutoff if possible or be sure enough pressure is maintained to prevent back-up.

1/ Conner, James T., "Report of the National Agricultural Chemicals Association," presented at the National Working Conference on Pesticide Disposal, Beltsville, Maryland (30 June and 1 July 1970).

C. Check flow of run-off water and make provisions to divert or dam up if flow constitutes undue hazard of exposure or pollution.

D. Check for possible exposure of food products to smoke or vapor. If so, advise public health officials.

E. Call the "Pesticide Safety Team Network" (513-961-4300) for all possible aid and assistance in decontamination and disposal.

F. Provide for the protection of personnel involved in the clean-up and decontamination of the area.

   1. Advise physician having a laboratory of possible types of exposure.

   2. In the event of involvement of organic phosphate compounds, arrange for blood tests for cholinesterase level for reference on all personnel at the site and anyone off-site who may be exposed. Arrange for periodic (at least weekly) retest.

   3. Provide necessary rubber boots, rubber or plastic gloves, rubber or plastic aprons or clothing and/or disposable clothing, suitable respirators or masks.

   4. Make arrangements for a supervised emergency showering and personnel hygiene program for showers and clothing changes prior to eating, smoking, drinking coffee or changing clothes prior to leaving the area.

Make preparations for disposal by burial of both contaminated building contents and building debris.

   1. Contaminated building contents

      a. Locate an area where quantities of material either pesticides or other items contaminated may be buried without danger of contaminating ground water or where surface water will not be contaminated.
      b. Arrange for test drilling to a depth of approximately 7 ft and have soil tested by a consulting engineer or soil conservation agency for porosity.
      c. If soil porosity is high or if in doubt, place 4 to 6 in. of powdered attapulgus-type clay as a lining in the burial trench or pit.

d. Material must be transported to burial site in closed containers to avoid contamination enroute and preferably buried in these containers at the site.
e. A cover of 2 to 3 in. of lime and a minimum of 18 in. of dirt cover must be placed and compacted over each load immediately after being placed in the pit or trench.
f. Each load deposited and covered should be supervised by a responsible company employee or a public health official.
g. After disposal is completed, the area should be marked and properly recorded on a plat of the area.

2. Contaminated building debris

a. Building ashes, wood, brick, stone, etc., may be disposed of by using ordinary sanitary land fill techniques.
b. Debris must be transported in covered trucks to prevent contamination during transport if burial on site not possible.
c. All debris must be covered with a minimum of 6 in. of dirt each day.
d. Area selected must be such that ground or surface water will not be contaminated.

3. A check with local authorities must be made for regulations governing this type of disposal. All governing regulations must be followed and the procedures above are intended to augment and not supersede these regulations.

H. Area decontamination

1. A check of the recommendations for decontamination of the area after debris removal with a representative of the "Pesticide Safety Team Network" must be made.

2. A check must be made with the supplier regarding the decontamination recommendations.

3. In lieu of a firm recommendation, the contaminated area may be tested for contamination and grossly contaminated areas wet down with a 1% solution of bleach or if concrete scrubbed down with a 1% bleach solution and rechecked for contamination. This procedure is repeated until contamination is at a low level.

I. Arrangements should be made to provide around-the-clock watchman service to prevent sightseers and scavengers from exposure until disposal and decontamination is complete.

APPENDIX C

PRELIMINARY DISCHARGE DATA SUBMITTED BY PESTICIDE PRODUCERS UNDER THE 1899 REFUSE ACT

Under the "1899 Refuse Act Permit Program," industries are required to obtain permits to make discharges into navigable waters or their tributaries. Companies have recently been required, under the new enforcement of this act, to submit applications describing the nature of their discharges. The applications, which are submitted to the Corps of Engineers and are to be reviewed by the Environmental Protection Agency, were to be made in two parts: Part A was required of all companies having discharges and describes facilities and the general nature of the discharge and was due in July 1971; Part B was required of companies in a critical industry classification, including pesticide producers and describes the quantitative nature of the discharge (including levels and amounts of specific pesticides) and was due in October 1971.

While many pesticide producers use other means of wastewater disposal, most are believed to come under the 1899 Act. Unfortunately, most of the data which will be contained in the Part B's of the applications did not become available in time to be included in this study. Copies of applications from only six companies were obtained. A small part of the pertinent data contained therein are shown in Table C-I.

TABLE C-I

PRELIMINARY DISCHARGE DATA SUBMITTED BY PESTICIDE PRODUCERS UNDER THE 1899 REFUSE DISPOSAL ACT

Company and Plant Location	Active Ingredient and Related Products	Loss (lb/day)	Total Discharge (MM gal/day)	pH	Remarks
Chemagro Corp., Kansas City, Missouri	Monitor	-			Dashes indicate not being produced at time o analysis
	Guthion	7	0.32	8	
	Dasanit	-			
	Coumaphos	3			
	Systox	5			
	Meta-Systox	-			
	Dyrene	-			
	Fenthion	-			
	Di-Syston	19			
Ciba-Geigy, St. Gabriel, Louisiana	Atrazine Propazine Simazine	2,300	5.5	11.5	Projected for full capacity operation
Diamond Shamrock, Deer Park, Texas	Dacthal		0.334	6.9	
	MSMA				
	DSMA				
Du Pont, La Porte, Texas	Diuron	350	9.5	5.5-9.0	
	Monuron	310			
	Linuron	390			
	Thiuram	9			
Monsanto, Muscatine, Iowa	Alachlor	90	12.35	4.1	
	Machete	30			
	Propachlor	360			
	Methylchloroacetate	612			
Shell Chemical Company, Mobile, Alabama	Gardona	Max 0.02	0.175	12	
	Vapona	Max 1.0			
	Dibrom	Max 1.0			
	Landrin	Max 1.5			
	Temik	Max 1.0			

APPENDIX D

LIST OF INDIVIDUAL CONTRIBUTORS TO THIS STUDY

The assistance of the following individuals who generously contributed their time and information to this study is greatfully acknowledged.

Dr. Ralph F. Anderson
International Minerals and
Chemical Corporation

Mr. R. W. Arns
Chevron Chemical Company
Ortho Division

Mr. D. B. Barlow
Chevron Chemical Company
Ortho Division

Mr. Charles Barnett
Shell Chemical Company

Mr. Carl A. Bauer
Valley Chemical Company

Mr. William E. Baum
Abbott Laboratories

Mr. H. A. Beckman
Chevron Chemical Company
Ortho Division

Mr. J. H. Bees
Union Carbide Corporation

Mr. Bill Bell
Arlington Blending and
Packaging Company

Mr. Edsel H. Blair
Dow Chemical Corporation

Mr. Charlie Blue
Helena Chemical Company

Mr. Parke C. Brinkley
National Agricultural
Chemists Association

Mr. William Brothers
Helena Chemical Corporation

Mr. George E. Brown
Mallinckrodt Chemical Works

Mr. Jack Buan
Abbott Laboratories

Mr. Henry (Hank) F. Clancy
American Cyanamid Company

Dr. E. L. Clark
Chipman Division
Rhodia, Inc.

Mr. Charles J. Coken
Chemagro Corporation

Mr. R. A. "Rip" Collins
Hercules, Inc.

Mr. Jack G. Copeland
Hercules, Inc.

Mr. D. Dick DeLine
Dow Chemical Corporation

Mr. Charles L. Dunn
Hercules, Inc.

Mr. M. A. Eggleton
Mallinckrodt Chemical Works

Mr. Tom Engerson
FMC, Niagara Chemical Division

Mr. John Ferguson
Geigy Agricultural Chemicals
Division of Ciba-Geigy

Dr. W. Brooks Fortune
Elanco Products Division of
Eli Lilly and Company

Dr. Frank Fronec
E-Z Flow Chemicals, Division of
Kirsto Company

Mr. E. A. Gilbert
FMC, Niagara Chemicals Division

Mr. Joe W. Gillespie
Monsanto Company

Mr. H. M. Godson
Calhio Chemical, Inc.

Mr. Don Gohlson
Cook Chemical Company

Mr. Harvey Gresheim
Coahoma Chemical Company

Mr. William H. Gurnee, Jr.
Ciba-Geigy Corporation

Mr. Bob Hamman
Geigy Agricultural Products
Division of Ciba-Geigy

Mr. Willis H. Hart
Thompson-Hayward Chemical Company

Dr. Friedrich Hellrung
Chemagro Corporation

Mr. George G. Hinkson
FMC-Niagara Chemical Division

Mr. Loren J. How
Agricultural Division
Stauffer Chemical Company

Dr. Herbert E. Johnson
Union Carbide Corporation

Mr. John L. Kallok
Montrose Chemical Corporation

Mr. D. J. Keating
Stauffer Chemical Corporation

Mr. Douglas Kelly
Riverside Industries, Inc.

Dr. Edward M. Kiggins
Abbott Laboratories

Mr. Peter J. Klaphaak
Union Carbide Corporation

Mr. J. Harvey Knaus
Shell Chemical Company

Mr. T. J. Koffolt
Union Carbide Corporation

Mr. Joe Langer
Chase Chemical Company

Mr. Dick Leonard
Hercules, Inc.

Mr. Donald Lloyd
Wilbur-Ellis Corporation

Mr. Bruce MacDonald
Pulvair Corporation

Mr. Paul Manfredi
Wilbur-Ellis Corporation

Mr. Bob Mathews
Velsicol Chemical Corporation

Mr. Russell W. McCalley
O. M. Scott Corporation

Mr. D. B. McClellan
McLaughlin Gormley and King Company

Mr. A. M. McVie
Elanco Products Division
Eli Lilly and Company

Dr. J. B. Moore
McLaughlin Gormley and King Company

Mr. Robert E. Naegele
Dow Chemical Corporation

Mr. Leonard W. Nelson
Velsicol Chemical Corporation

Mr. Bill Niggle
Chemagro Corporation

Mr. Jan Platou
The Sulphur Institute

Mr. Gene Renolds
FMC, Niagara Chemical Company

Mr. W. B. Roebird
Monsanto Company

Mr. Frank Saviez
Wilbur-Ellis Company

Mr. Bud Schroeder
Thompson-Hayward Chemical Company

Dr. Warren C. Shaw
U.S. Department of Agriculture

Mr. Max Sobelman
Montrose Chemical Corporation

Mr. Ed Spring
Gordon Corporation

Mr. John Stevens
Monsanto Company

Dr. Warren T. Trask
Mallinckrodt Chemical Works

Mr. John H. Vines
Chemagro Corporation

Mr. Edward B. Westall
Nutralite Products, Inc.

Mr. Tom J. White
American Cyanamid Company

Mr. Norman Zausmer
Michlin Chemical Corporation